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The
PALLADIUM
HYDROGEN
System

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The PALLADIUM HYDROGEN *System*

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ACADEMIC PRESS · 1967
LONDON NEW YORK

ACADEMIC PRESS INC. (LONDON) LTD
BERKELEY SQUARE HOUSE
BERKELEY SQUARE
LONDON, W.1

U.S. *Edition published by*
ACADEMIC PRESS INC.
111 FIFTH AVENUE
NEW YORK, NEW YORK 10003

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Library of Congress Catalog Card Number: 66-30129

Printed in Great Britain
by Richard Clay (The Chaucer Press), Ltd.,
Bungay, Suffolk.

Preface

The palladium/hydrogen system has been perhaps the most extensively experimentally investigated metal/gas system. It represents a particular example of a general problem in inorganic binary systems concerning departures of the composition of the solid phase from simple stoichiometric ratios dependent on temperature and the equilibrium pressure of the gaseous component.

The system has further specific interest in that even with high contents of hydrogen, the solid phase retains considerable mechanical robustness in addition to its retention of metallic appearance and the considerable electrical conductivity also broadly characteristic of other hydrides of the transition elements. From an academic standpoint, interest in the system has perhaps centred primarily around attempts to provide theoretical explanations both of the form in which the hydrogen is contained in the solid and of the form of the pressure–composition relationships.

Combinations of practical and theoretical interests have arisen from the applications of palladium and certain palladium alloys as hydrogen diffusion membranes, which also partly stems from their rather unique resistance to disruption and serious embrittlement even after absorbing large concentrations of hydrogen. These features of the systems can, furthermore, also prove of experimental advantage in investigations into the role of palladium (as well as of allied elements; for example, of the platinum group) in the fields of catalytic hydrogenation and of the evolution of hydrogen by electrolysis.

The Queen's University of Belfast. F. A. Lewis.
November, 1966.

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CHAPTER 1

General Introduction

A. Comparison of the Properties of Palladium with Those of Other Transition Elements

As indicated in the schematic periodic chart of the transition elements in Fig. 1.1, palladium is one of the nine elements commonly referred to

3		4	5	6	7	8			1	2
Sc		Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y		Zr	Nb	Mo	Tc	Ru	Rh	**Pd**	Ag	Cd
La	Rare earths	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
	Actinons									

Fig. 1.1 Sub-groupings of the transition elements.

as Group 8 of the periodic classification. Also it is one of the six elements of Group 8 in the second and third transition metal series, which are also commonly referred to as the "platinum metals".

In a vertical grouping, palladium is intermediate between nickel and platinum itself—all three of these elements being among those most commonly employed as catalysts for hydrogenation reactions.

Geologically, all six platinum metals generally occur in conjunction with one another. In addition to specifically platiniferous ores, a further workable source is provided by the by-products of nickel refining. Although there can be substantial variations in relative proportions, in general platinum itself forms the largest fraction of the final precious metal concentrates, with palladium as the next most abundant element. Alloy mixtures of the platinum metals have been known for several centuries but it was not until the 19th century that Woolaston and Tennant succeeded in isolating the individual elements.

Table 1.1 lists various physical properties of the platinum metals and

TABLE 1.1

Some properties of the platinum metals[1]

	Ruthenium	Rhodium	Palladium	Osmium	Iridium	Platinum
Atomic number	44	45	46	76	77	78
Atomic weight	101·07	102·9	106·4	190·2	192·2	195·1
Crystal structure	h.c.p.	f.c.c.	f.c.c.	h.c.p.	f.c.c.	f.c.c.
Lattice constant at 20° C — kx units (1 kx = 1·00202 A)	—	3·7963	3·8829	—	3·8317	3·9152
Density at 20° C g/cm³	12·45	12·41	12·02	22·61	22·65	21·45
Melting point (°C)	2310	1960	1552	3050	2443	1769
Boiling point (°C)	4100	3700	2900	5000	4500	3800
Electrical resistivity at 0° C (micro-ohm/cm)	6·80	4·33	9·93	8·12	4·71	9·85
Temperature coefficient of electrical resistance (0–100° C) per °C	0·0042	0·0046	0·0038	0·0042	0·0043	0·0039
Magnetic susceptibility at 18°C (c.g.s. units × 10⁶)	0·50	1·11	5·4	0·05	0·15	1·10
Young's Modulus lb/in² × 10⁻⁶	60	46·2	16·7	81	75	24·8
Hardness (DPN) for annealed specimens	250–450	120	37–40	330–760	200–240	37–42

[1] After International Nickel Co. Ltd., technical bulletins and Anon. (1957); cf. *Platinum Metals Rev.* **1**, 61; cf. Darling (1966).

it may be seen that palladium has the lowest melting point and density of the group, but that it has a markedly higher magnetic susceptibility. As may be expected from its lower melting point, palladium has a higher vapour pressure than the other platinum metals over the range of temperatures up to its melting point, and an accompanying lower heat of vaporization (e.g., Darling, 1964a, 1966). A further general property which somewhat differentiates palladium is that it is rather less resistant to chemical attack by common acids, such as nitric and sulphuric, than the other platinum metals.

B. Permeation of Hydrogen Through Transition Elements—"Occlusion" by Palladium

The first observations of the permeability to hydrogen of transition metals appear to have been made by Deville and Troost, whose experiments were carried out on iron and platinum (Deville and Troost, 1863; Deville, 1864). Thomas Graham carried out related measurements quite soon afterwards. By this time palladium was available in sufficient quantities for Matthey to be able to fabricate a tube of the metal to act as a septum, and Graham soon observed that not only did palladium permit high throughputs of hydrogen, but that large volumes of hydrogen were absorbed by, or as Graham termed it "occluded" by, the tube when it was allowed to cool to room temperature in an atmosphere of hydrogen (Graham, 1866).

Since that time probably a larger number of experimental investigations have been carried out concerning the absorption of hydrogen by palladium than have been carried out with any other metal/gas system. This reflects a sustained academic interest in the reasons for the high solubility of hydrogen in palladium compared with other elements over a very wide range of temperature and pressures of hydrogen gas. It also reflects the practical importance of the accompanying high rates of permeation of hydrogen through palladium when compared to membranes of the same thickness of the other metals at the same temperature and with the same pressure gradients. The interrelationship between the solubility and diffusibility of hydrogen in palladium are discussed in more detail in Chapter 7.

On occasions other metals have been preferred as diffusion membranes for hydrogen under certain circumstances. Nickel, for example, sometimes has been preferred to palladium—generally on grounds of expense—and at higher temperatures iridium was used in Nernst's classical studies of gaseous equilibria involving hydrogen. Moreover, extensive industrial applications have been somewhat curtailed because

of the distortion of palladium membranes which can occur in service under fairly wide ranges of experimental conditions with regard both to temperature and to pressures of gas.

There has, however, been a steadily increasing demand for hydrogen of high purity. This has been paralleled by the use, instead of pure palladium, of certain ranges of composition of Pd/Ag and Pd/Au alloys. These combine increased resistance to this deformation with an increased permeability under certain conditions (see Chapters 3, 6 and 7).

C. Pressure–Composition–Temperature (p–C–T) Relationships: Non-Stoichiometry

In latter years, the primary academic concern with the palladium/hydrogen system has probably been with attempts to account for the form of the isothermal pressure–composition relationships derived in solid/gas equilibration studies. Measurements of this type have been obtained at intervals since the study by Deville's co-worker Troost in collaboration with Hautefeuille in 1874. The diagrammatic plot in Fig. 1.2 corresponds with the more comprehensive relationships derived by Gillespie and by Sieverts and their collaborators in the 1930s.

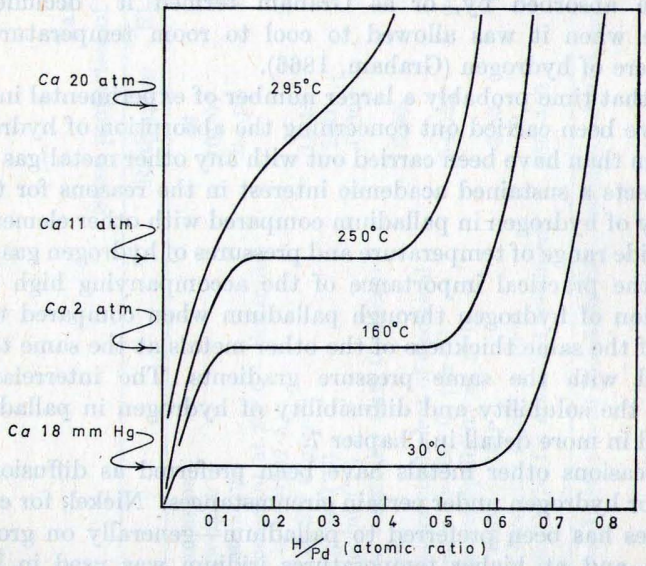


Fig. 1.2 Schematic diagram of absorption relationships between equilibrium vapour pressure and hydrogen content after Brüning and Sieverts (1933), Gillespie and Galstaun (1936) and Wicke and Nernst (1964).

The trend in the change in the form of the isotherms with changes of temperature is quite analogous to trends in the isotherms representing the changes in volume of real gases as a function of pressure. In the case of compressions of a gas, the critical isotherm, of course, corresponds to the temperature boundary dividing the possibility or impossibility of liquefaction. Above the critical temperature in the case of the Pd/H system, two solid hydride phases of differing composition cannot exist together in the solid under steady-state conditions at any hydrogen content. Below the critical temperature the regions over which the so-termed α- and β-phase hydrides of the system can co-exist, is represented by the horizontal, pressure invariant, portion of the isotherm.

The chemical composition of the β-phase hydride over the region of co-existence of α- and β-phase hydrides corresponds with the composition at the second "break" in the isotherm. It is clear from Fig. 1.2 that this composition varies continually with temperature and that, in general, there is no simple ratio of hydrogen atoms to palladium atoms in either this or in the α-phase hydride. This general non-stoichiometry of composition of the hydride phases, and in particular of the β-phase, was for some time believed to constitute a unique case; but latterly the families of isotherms of many solid/gas systems have been found to exhibit analogous trends where data are sufficiently comprehensive for this to be revealed.

D. Introduction of Hydrogen into Palladium by Electrolysis

The absorption of hydrogen by cathodes of palladium during electrolysis also first seems to have been reported by Thomas Graham (1868). In the same paper, Graham also noted that hydrogen could be removed again from the hydrided cathode if the polarity of the cell was reversed so that the palladium electrode then became the anode. These "electrolytic" methods have often been employed since for the introduction (particularly into alloys of the palladium/silver series) or removal of controlled amounts of hydrogen—although the methods of pre-activation of the surfaces of the specimens must still be regarded as largely empirical.

In general, measurements of electrode potential have only rarely been carried out in conjunction with the majority of these studies. It is thus not possible to make a thermodynamic correlation or cross-check with values of equilibrium vapour pressure at the same value of hydrogen content as determined in pressure–concentration (p–C) relationships

obtained in solid/gas phase equilibrium studies. However, it is only recently that arguments concerning these thermodynamic correlations have been broadly resolved. It seems fairly clear, as a result of the controversy, that even if measurements of electrode potential had been available in the earlier work it is doubtful how far they could be relied upon—since it has been emphasized in more recent work how sensitive the value of electrode potential is to the state of activation of the surface with regard to its ability to equilibrate with hydrogen molecules dissolved in the electrolyte.

Furthermore, many studies using the "electrolytic" method for introduction and removal of hydrogen have also been carried out without sufficient awareness of other sources of experimental error. All of these factors will be considered in more detail in Chapters 2, 4 and 6.

A general upshot of these considerations is that a large percentage of measurements (particularly concerning relative solubilities of hydrogen in various alloys) obtained by the electrolytic method have proved of little quantitative value. In fact, unfortunately, many arbitrary measurements of solubility without reference to electrode potential (and so pressure) have proved quite misleading and given rise to rather barren controversy—for example, particularly with regard to the solubility of hydrogen in the palladium/silver series of alloys (see Chapter 6).

E. General Comparison of the Solubility of Hydrogen in Other Transition Elements

It can hardly be overemphasized that when making comparisons of the solubility of hydrogen (or the possibility of the formation of hydrides) by various metals it is not only essential that there should be a uniform equilibration of hydrogen throughout the solid but also that the comparison should be qualified with respect to the temperature of measurement and to the pressure of hydrogen gas. Unfortunately, vague or even incorrect generalizations often have been made without regard to such qualifications. In particular, erroneous statements have arisen when quoting solubilities recorded under non-equilibrium conditions such as may occur, for example, when hydrogen is introduced by electrolysis as already mentioned above.

F. Solubility of Hydrogen in Other Elements of Group 8

Although few data are available for some of these elements, it seems fairly certain that the "solubility" of hydrogen in palladium markedly

exceeds that in the other elements in Group 8 over a very wide range of temperatures and pressures. Comparisons of solubilities available for some of the elements in Group 8 are shown in Fig. 1.3.

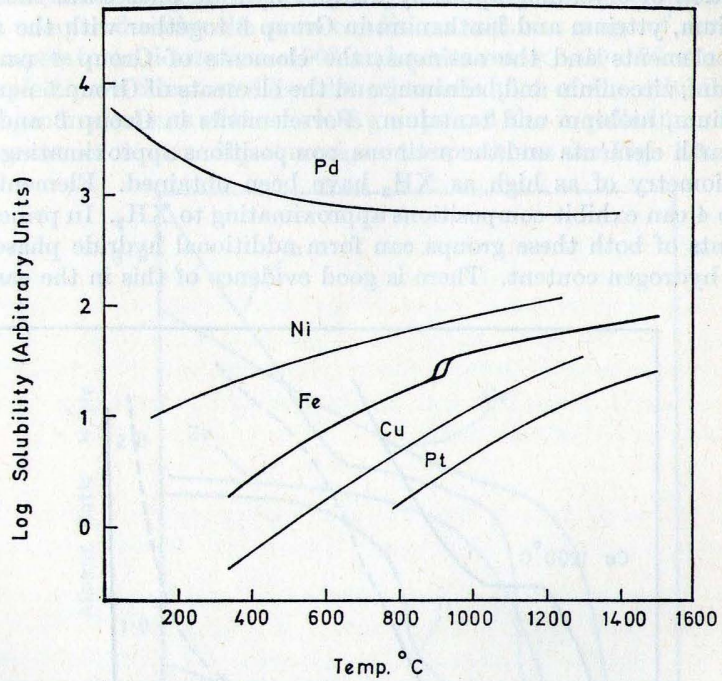


Fig. 1.3 Schematic comparison of solubility of hydrogen in Group 8 metals at a pressure of 1 atm as a function of temperature—after Borelius (1927) as compiled from data of Sieverts, cf. also Kubaschewski (1938).

In general it also seems that it is only for palladium (and also probably for nickel in equilibrium with very high pressures of hydrogen gas), and then only at temperatures below ~300°, that there is crystallographic evidence (or evidence from the existence of regions of pressure invariance in isothermal plots of hydrogen vapour pressure against composition) of the major lattice rearrangements corresponding with the phase transformations characteristic of the formation of a specific hydride phase. This is as distinct from what seem likely to be no more than the local distortions around the solute atoms which probably occur in what are termed solid solutions.

G. Absorption of Hydrogen by Transition Elements of Groups 3, 4 and 5

The other transition elements for which there is sound evidence of the formation of crystallographically distinct hydride phases are those of scandium, yttrium and lanthanum in Group 3 together with the rare-earth elements and the actinons; the elements of Group 4 namely titanium, zirconium and hafnium; and the elements of Group 5 namely vanadium, niobium and tantalum. For elements in Group 3 and the rare-earth elements and the actinons, compositions approximating to a stoichiometry of as high as XH_3 have been obtained. Elements in Group 4 can exhibit compositions approximating to XH_2. In principle, elements of both these groups can form additional hydride phases of lower hydrogen content. There is good evidence of this in the case of

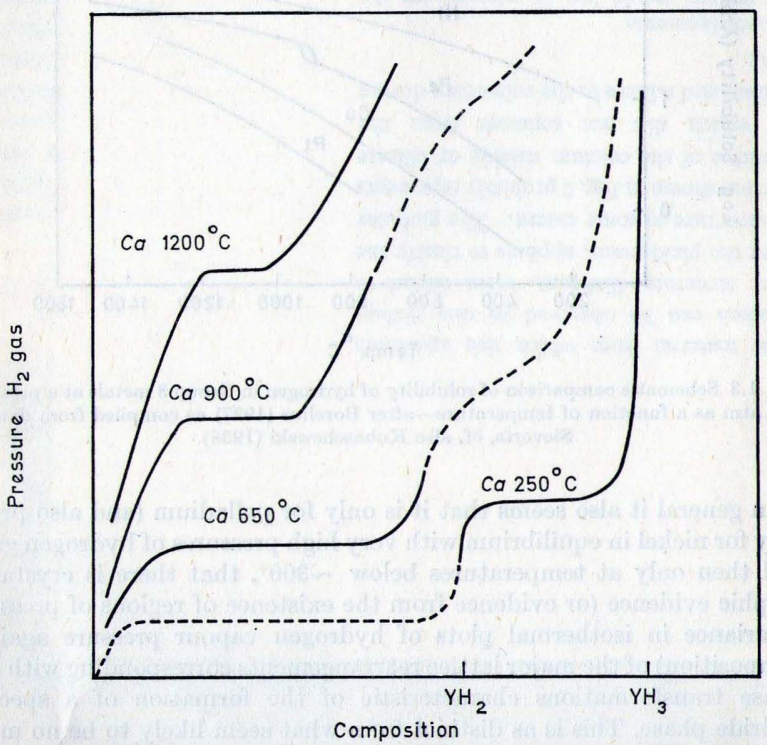


Fig. 1.4 Schematic plots of isotherms of the Y/H system as an example of a transition metal/hydrogen system which exhibits evidence of more than one phase transformation —after Lundin and Blackledge (1962), Yannopoulos *et al.* (1965), cf. La Grange *et al.* (1959).

the zirconium/hydrogen system (La Grange *et al.*, 1959) and in the case of the yttrium/hydrogen system (Lundin and Blackledge, 1962) (Yannopoulos *et al.*, 1965) as indicated diagrammatically in Fig. 1.4. With increasing group number from 3 to 5 there is a complementary decrease in the highest ratio of hydrogen to metal in the resultant solid when compared under the same conditions within a range of variables of temperatures down to ~100° and pressures < ~10–100 atm. By example this is illustrated by the schematic plot of the solubility of hydrogen in elements of the various groups and also in palladium, under a pressure of 1 atm H_2 at various temperatures in Fig. 1.5. This

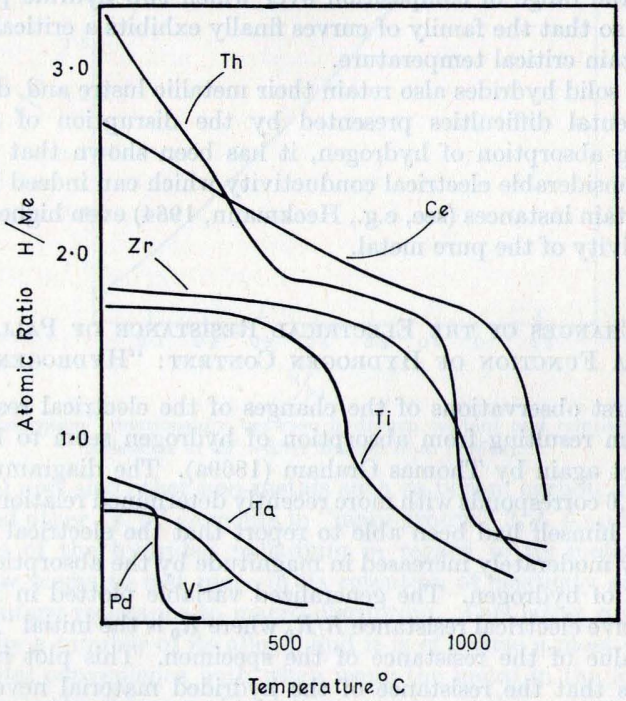


Fig. 1.5 Illustrations of the temperature dependence of the contents of hydrogen absorbed, in equilibrium with hydrogen gas at atmospheric pressure, by some transition elements which can form crystallographically distinct hydride phases—after Sieverts (1929), cf. Smith (1948).

illustrates that the content of hydrogen in the element of Group 5 (V, Nb, Ta) is comparable over this range of conditions with the solubility in palladium.

Over the last twenty years or so increasingly detailed pressure–composition–temperature relationships of the absorption of hydrogen

by these elements have been determined. Quite comprehensive reviews of this information have been compiled fairly recently (Libowitz, 1960, 1963, 1965; Mikheeva and Kost, 1960; Gibb, 1962b; Mackay, 1966).

The formation of hydrides by these elements provides certain analogies with the palladium/hydrogen system. For instance, isothermal pressure–composition plots exhibit families of curves with similarities in that ranges of pressure invariance can be obtained as shown in Fig. 1.4 which correspond to the co-existence of hydride phases with marked deviations from a simple stoichiometric composition. Moreover, with increase in temperature there is a steady diminution in the range of composition over which two hydride phases can co-exist so that the family of curves finally exhibits a critical isotherm at a certain critical temperature.

These solid hydrides also retain their metallic lustre and, despite the experimental difficulties presented by the disruption of specimens following absorption of hydrogen, it has been shown that the solids retain considerable electrical conductivity which can indeed be as high or in certain instances (see, e.g., Heckmann, 1964) even higher than the conductivity of the pure metal.

H. Changes of the Electrical Resistance of Palladium as a Function of Hydrogen Content: "Hydrogenium"

The first observations of the changes of the electrical resistance of palladium resulting from absorption of hydrogen seem to have been made yet again by Thomas Graham (1869a). The diagrammatic plot in Fig. 1.6 corresponds with more recently determined relationships, but Graham himself had been able to report that the electrical resistance was only moderately increased in magnitude by the absorption of large volumes of hydrogen. The generalized variable plotted in Fig. 1.6 is the relative electrical resistance R/R_0 where R_0 is the initial "hydrogen-free" value of the resistance of the specimen. This plot in Fig. 1.6 indicates that the resistance of the hydrided material never exceeds twice that of the original palladium, although the actual increase of resistance would be slightly more if comparisons were made in terms of "specific" electrical resistance—i.e., taking account of the concurrent relatively small increase in the dimensions of the specimen. Nevertheless, the plot clearly shows that the hydrided solids retain a very high electrical conductivity which encouraged Graham to suggest that the hydrogen in the palladium behaved as a metallic alloy, so that he termed hydrogen in this form "hydrogenium". He was encouraged in this viewpoint by the retention by the hydrided palladium of both a metallic

appearance and of a considerable ductility. More recently, however, both considerable electrical conductivity and metallic lustre also have been found to be retained by many other compounds of the transition elements both with hydrogen (as discussed above for elements in Groups

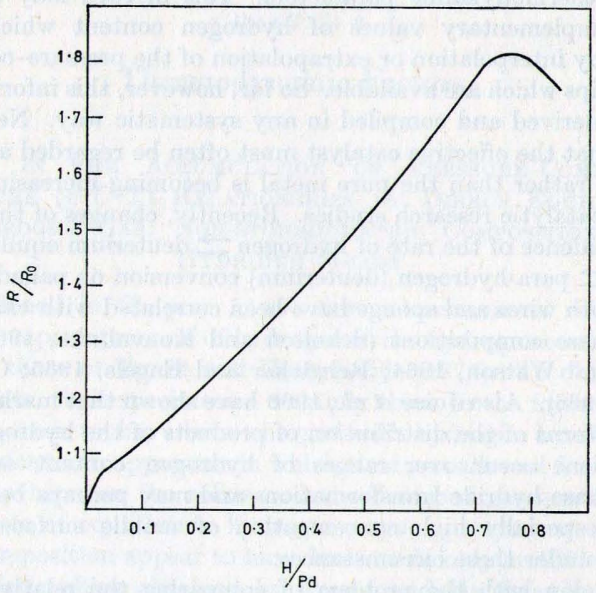


Fig. 1.6 "Absorption" relationships between hydrogen content and relative electrical resistance at 25°—after Barton *et al.* (1963a).

3, 4 and 5) and also other non-metals such as boron, carbon, nitrogen, oxygen and other "s, p" elements in "main-groups" 3, 4, 5 and 6. Any uniqueness of the hydrided palladium in regard to its metallic properties now seems to rest more in its retention of elasticity and in its complementary resistance to macro-disruption. This latter ruggedness is shared by a number of its alloys, and it is of course a most valuable experimental convenience both when using the metal in the form of a membrane for the diffusion of hydrogen, or when making measurements of changes in physical properties as a detailed function of changes of hydrogen content.

I. The Introduction of Hydrogen into Palladium in the Course of Chemical Reactions: Palladium as an Hydrogenation Catalyst

Together with its congener elements nickel and platinum, palladium is widely employed as a catalyst in chemical reactions—most

particularly perhaps in hydrogenations. During such reactions some hydrogen is almost certainly absorbed by the palladium depending on the temperature and on the effective concentration of hydrogen gas. In principle, the latter concentration often may be calculated from available thermodynamic parameters. This in turn may be used to derive complementary values of hydrogen content which may be obtained by interpolation or extrapolation of the pressure–composition relationships which are available. So far, however, this information has not been derived and compiled in any systematic way. Nevertheless, the fact that the effective catalyst must often be regarded as hydrided palladium rather than the pure metal is becoming increasingly appreciated in catalytic research studies. Recently, changes of the temperature dependence of the rate of hydrogen $\rightleftarrows$ deuterium equilibrium and of ortho $\rightleftarrows$ para-hydrogen (deuterium) conversion on palladium in the form of both wires and sponge have been correlated with changes from α- to β-phase compositions (Scholten and Konvalinka, 1966; cf. also Schwab and Watson, 1964; Reinäcker and Engels, 1965; Couper and Metcalf, 1966). Also Joice *et al.*, 1966 have shown that marked changes in the patterns of the distribution of products of the hydrogenation of 1,3-butadiene occur over ranges of hydrogen content adjacent to α- $\rightleftarrows$ β-phase hydride transformations and may perhaps be associated with an especially high concentration of mobile surface-species of hydrogen under these circumstances.

In common with the problem of comparing the relative catalytic activity of different metals, it is difficult to obtain surfaces which provide a reliable reference state, since catalytic activity is so much a function both of the pre-treatment and of further physical and/or chemical changes due to the conditions of the experiment. Thus in trying to gauge effects due to changes in hydrogen content, it seems as necessary to have some guide to the surface condition of the specimen as it is to have a knowledge of its bulk hydrogen content.

When the catalyst (palladium) is in the finely divided or dispersed form in which it is employed in many important practical circumstances, virtually the only method of estimating the hydrogen content is through the considerations of chemical equilibria referred to above. However, with more massive and continuous specimens such as wires, for instance, the hydrogen content can also be estimated from the value of some physical property such as electrical resistance which can be measured relatively conveniently and for which fairly detailed relationships with hydrogen content have been derived (see Chapters 4 and 5).

CHAPTER 2

Thermodynamic Factors

A. Stages in the Accumulation of Pressure–Composition–Temperature (p–C–T) Relationships by Direct Equilibration with Hydrogen Gas: Non-stoichiometric Composition of the Hydrided Solids

As mentioned in Chapter 1, the first measurements relating the equilibrium vapour pressure of hydrogen to the hydrogen content of the solid, were those of Troost and Hautefeuille (1874). To obtain these measurements, their specimens—certainly those in the form of "cast" palladium—seem to have been charged with hydrogen by electrolysis before transfer to an apparatus in which time was allowed for equilibria to be set up between the solids and the desorbed gaseous hydrogen. Measurements of equilibrium hydrogen vapour pressure at *more than one* solid composition appear to have been made only at 100° and 160°, and the relationships obtained by Troost and Hautefeuille at these temperatures are included in Fig. 2.1. Measurements at both temperatures indicated that there were ranges of composition over which the equilibrium vapour pressure remained virtually constant. In the case of the 100° isotherm there was evidence that the equilibrium pressure increased substantially at hydrogen contents greater than a composition which corresponded roughly to a palladium : hydrogen ratio of two : one, and Troost and Hautefeuille concluded that a hydride had been formed with the stoichiometric formula Pd_2H. These authors also recorded measurements of the value of the vapour pressure where it remained constant at other temperatures within the range 20–170°.

In 1895, Hoitsema published the results of a much more comprehensive series of measurements which had been obtained over a temperature range of 10–250° and (in the case of some measurements at higher temperatures) at pressures of hydrogen up to ~6 atm. Hoitsema not only reported the results of his own measurements, which had been obtained with palladium in the form of a finely divided powder (loosely termed palladium black) as well as some measurements obtained at 100° with palladium foil, but also earlier results obtained in 1890 by

Roozeboom using palladium "sponge" (probably a rather coarse grit). Roozeboom had indeed derived two series of relationships using somewhat different experimental techniques; one series (termed R_1) was in overall agreement with the relationships obtained by Hoitsema as

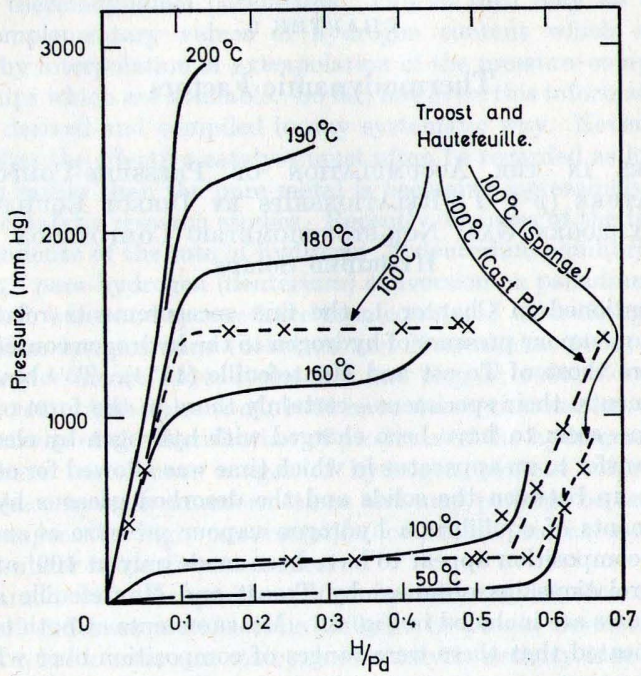


FIG. 2.1 Examples of p–C relationships derived by Hoitsema (1895) using palladium black.

indicated in Fig. 2.1—which is a reproduction of Hoitsema's Fig. 7 with measurements of Troost and Hautefeuille (which also are tabled in Hoitsema's paper) included for comparison. In Roozeboom's rather more comprehensive series of measurements (R_2) the hydrogen contents at the upper limits of the range over which the pressure remains constant, are substantially lower than those reported by any subsequent investigators.

Taken overall, however, while confirming Troost and Hautefeuille's findings of regions of hydrogen content over which the pressure remained virtually constant, Hoitsema and Roozeboom's results indicated that with change of temperature there was an accompanying change in the range of composition over which the pressure remained virtually constant. This virtually invalidated Troost and Hautefeuille's postulate

of the formation of Pd_2H which could be regarded as an oversimplification originating merely because of the fortuitous (from this point of view) form of the isotherm at 100°.

Hoitsema and Roozeboom's alternative interpretation of the form of the isotherms was that they corresponded to the formation of two ranges of solid solution of hydrogen in two solid phases which could each contain varying contents of hydrogen, but which were in some way structurally different from one another and, by analogy with phase rule terminology for liquids, could be described as immiscible with one another over ranges of hydrogen content where the pressure remained invariant.

Problems of interpreting the structures of the two phases more precisely will be discussed further in Chapters 9 and 10. However, for purposes of characterizing an isotherm which exhibits a region of virtual invariance of pressure, the form of changes of pressure with increasing hydrogen content can be divided into three stages and described in rough terms of the Hoitsema–Roozeboom interpretation somewhat after the following fashion:

At low hydrogen contents the equilibrium pressure shows a continuous increase. In this region the solid can be regarded as a solid solution of hydrogen in the original palladium lattice, and has become designated the α-phase[1] of the Pd/H system.

The hydrogen content at and above which the pressure remains constant corresponds with the maximum solubility of hydrogen in the α-phase structure and has become quite widely termed α_{max} (Flanagan and Lewis, 1959; Wicke and Nernst, 1964). It also represents the concentration above which a new hydride phase begins to nucleate. This has become known as the β-phase. The subsequent region of pressure invariance, or plateau region, corresponds to ranges of hydrogen content where α- and β-phase hydrides exist together in conjunction in the solid. As the hydrogen content increases over this region there is a continuous transformation from α- to β-phase.

Finally, when the phase transformation has been completed, the hydrogen vapour pressure once again begins to increase complementarily with further increases in hydrogen content. This third region

[1] It may perhaps be noted here that there have been suggestions, from results obtained at fairly low temperatures, that in α-phase regions of composition, the hydrogen is merely adsorbed on the surface (Cohen and de Bergevin, 1958) (cf. also Suhrmann, *et al.*, 1959). However, there is substantial evidence that this view is generally incorrect. This contradictory evidence includes the good agreement obtained between the p–C relationships derived for specimens of many different surface areas, the form of changes of electrical resistance with hydrogen content (see Lindsay and Pement, 1962), and the form of changes of lattice parameters with hydrogen content over a wide range of temperature (see, e.g., Maeland and Gibb, 1961).

is regarded as corresponding with the solution of further hydrogen in the β-phase hydride. The composition at the end of the region of pressure invariance corresponds to or at least approximates, the composition of the β-phase regions as formed initially and has been quite widely termed β_{min} (Wicke and Nernst, 1964).

However, for some considerable time subsequent to Hoitsema's paper there was reluctance to acknowledge the general non-stoichiometric composition of the solids.

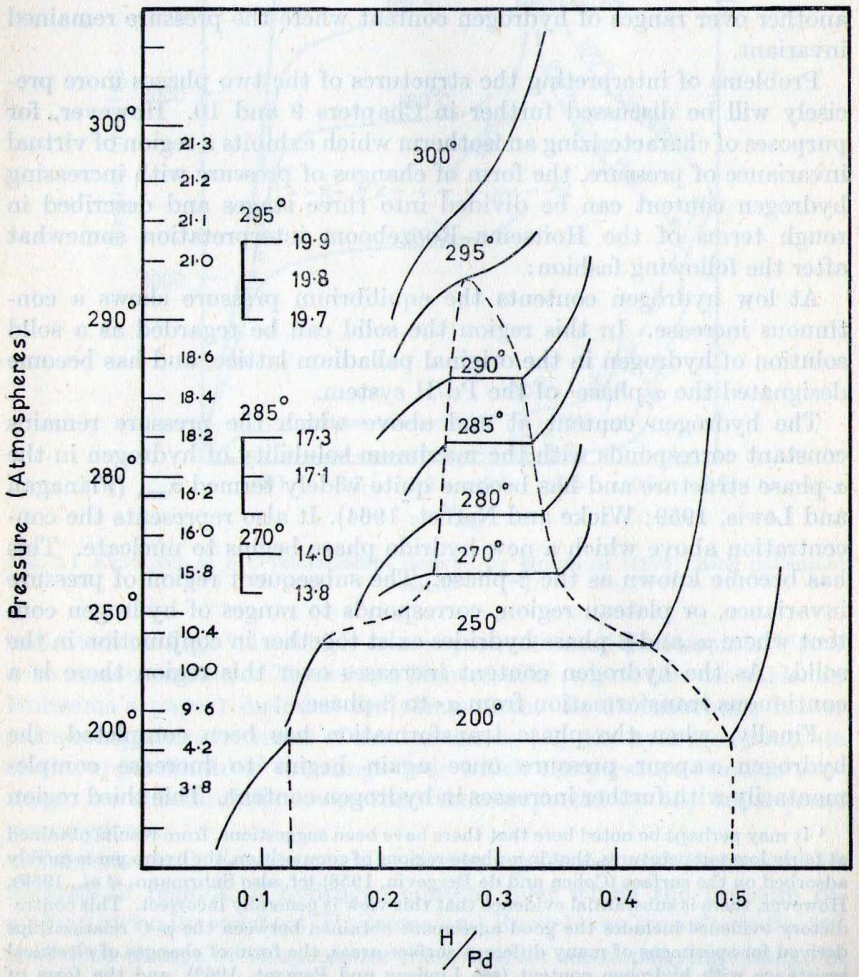


FIG. 2.2 Plots of p–C relationships after Gillespie and Galstaun (1936)—note discontinuous pressure scale and compare Fig. 1 of Moon (1956).

In particular, Gillespie—who, with his collaborators, has reported a substantial quantity of p–C–T data—not only interpreted results obtained with Hall (1926) as confirmatory evidence for Troost and Hautefeuille's postulate of the existence of Pd_2H but also interpreted

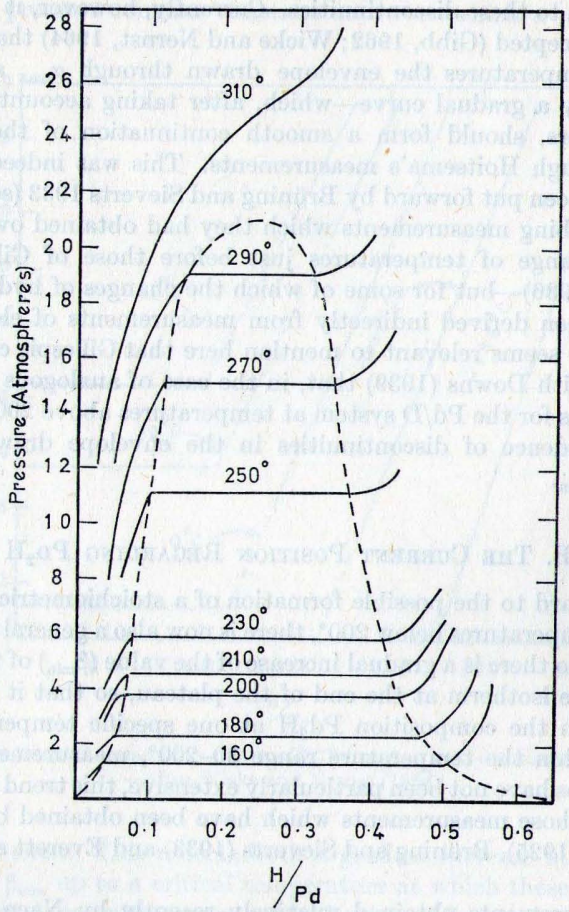


FIG. 2.3 Plots of p–C relationships—after Brüning and Sieverts (1933).

results obtained with Galstaun in 1936 as indicating the formation of other "compounds" with "chemical individuality" with formulae Pd_3H, Pd_4H and Pd_8H at temperatures between *ca* 200° and 300°. It was claimed that the formation of these compounds was suggested because there were corresponding discontinuities in the envelope drawn

through α_{max} and β_{min} for successive isotherms. This seems to have been rather misleadingly accentuated by Gillespie and Galstaun by leaving gaps in the range of values forming the pressure axis as indicated in Fig. 2.2. Unfortunately, the outline of the envelope in this figure has been redrawn by other authors, see, e.g. Moon (1956), without attention being drawn to these discontinuities. Currently, however, it now seems generally accepted (Gibb, 1962; Wicke and Nernst, 1964) that over this range of temperatures the envelope drawn through α_{max} and β_{min} is described by a gradual curve—which, after taking account of experimental errors, should form a smooth continuation of the envelope drawn through Hoitsema's measurements. This was indeed the view which had been put forward by Brüning and Sieverts 1933 (see Fig. 2.3) when describing measurements which they had obtained over roughly the same range of temperatures just before those of Gillespie and Galstaun (1936)—but for some of which the changes of hydrogen content had been derived indirectly from measurements of electrical resistance. It seems relevant to mention here that Gillespie conceded in his paper with Downs (1939) that, in the case of analogous isothermal relationships for the Pd/D system at temperatures above 200°, he could find no evidence of discontinuities in the envelope drawn through α_{max} and β_{min}.

B. The Current Position Regarding Pd_2H

With regard to the possible formation of a stoichiometric compound Pd_2H at temperatures below 200°, there is now also a general acceptance that here too there is a gradual increase of the value (β_{min}) of the upward break of the isotherm at the end of the plateau, so that it only corresponds with the composition Pd_2H at one specific temperature. Although within the temperature range 30–200°, measurements of p–C relationships have not been particularly extensive, this trend seems to be shown by those measurements which have been obtained by Lambert and Gates (1925), Brüning and Sieverts (1933) and Everett and Nordon (1960).

In measurements obtained relatively recently by Nace and Aston (1957) at 30°, it was found that β_{min} definitely exceeded 0·5, so that it is perhaps unfortunate that these authors reported accompanying calculations of thermodynamic parameters in terms of the composition Pd_2H, since this tends to keep alive the idea that this composition has some fundamental significance. The results of a recent study by Wicke and Nernst (1964) have provided clear evidence of gradual changes of both α_{max} and β_{min} within the temperature range −78·5–50°. The

relationships which they presented are reproduced in Fig. 2.4 (see also Fig. 2.12).

Thus to resummarize the position, the bulk of current evidence and opinion indicates that above −78·5° there is a gradual decrease without abrupt discontinuities in the range of contents over "plateau" regions where the pressure remains constant and over which α- and β-phase

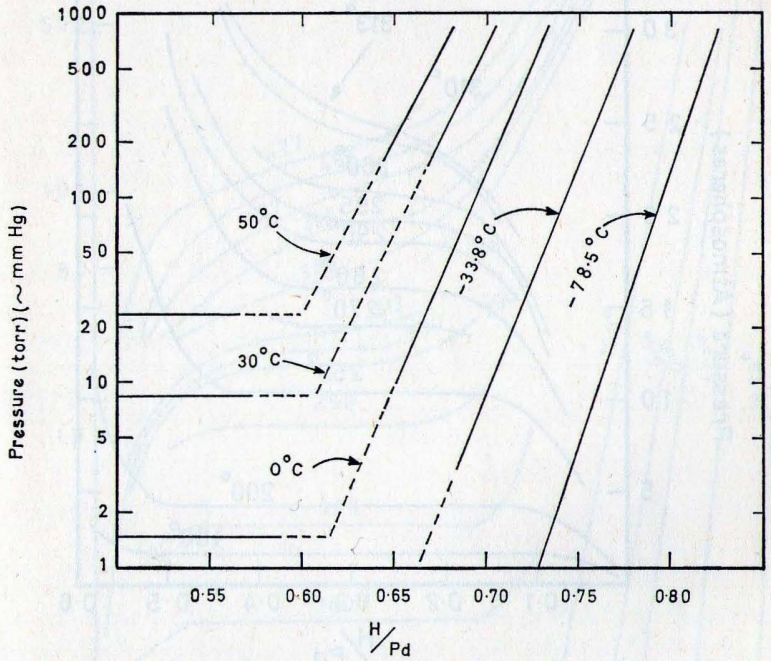


Fig. 2.4 Indications of a gradual increase of H/Pd at β_{min} with decreasing temperature —after Wicke and Nernst (1964).

hydrides co-exist. This reflects both a gradual increase in α_{max} and a decrease of β_{min} up to a critical temperature at which these points are coincident at a complementary critical composition and critical pressure. Evidence of the existence of such a critical isotherm at ~300° was first presented by Brüning and Sieverts (1933) and its existence was confirmed by Gillespie and Galstaun (1936) who made measurements at up to 313° and ~30 atm pressure of hydrogen and who gave values of 295·3° for the critical temperature, T_c, with values of 19·87 atm and H/Pd = 0·27 for the critical pressure, P_c and corresponding hydrogen content, respectively (see Figs. 2.2, 2.5 and 2.6). Since the value of

H/Pd corresponding with β_{min} at $-78{\cdot}5°$ is $\sim 0{\cdot}63$ (Wicke and Nernst, 1964), the value of 0·27 for H/Pd at the critical point reflects a slight asymmetry of the envelope of α_{max} and β_{min} in that it has a slightly steeper slope on the low hydrogen-content side.

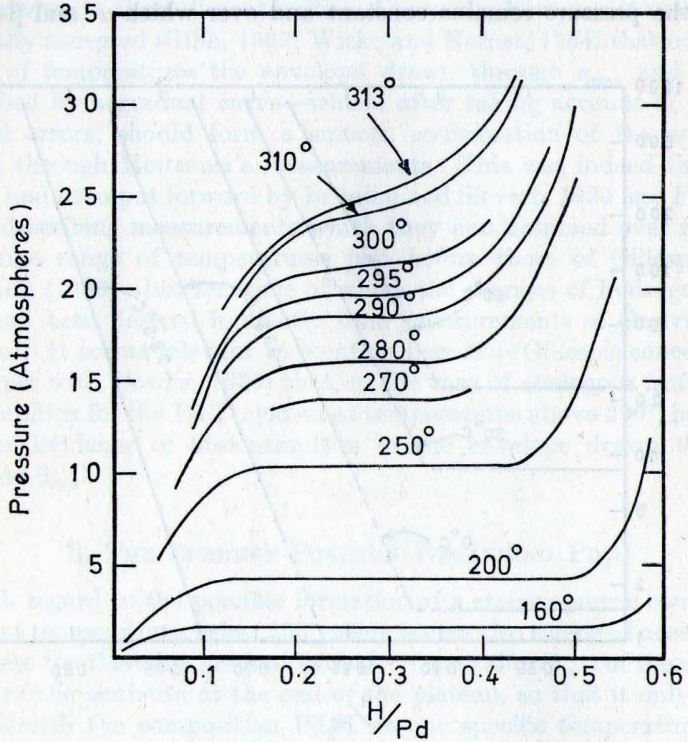


FIG. 2.5 Plots of p–C relationships at around T_c—after Gillespie and Galstaun (1936).

C. Relationships at Higher Temperatures than T_c

Quite detailed isothermal p–C relationships at temperatures higher than T_c (which may be termed "supercritical" isotherms) have been derived fairly recently by Levine and Weale (1960) for pressures up to $\sim$1000 atm (Fig. 2.6). These show that embryonic forms of the "two phase" plateau regions with accompanying substantial solubility of hydrogen are still clearly in evidence over the whole range of temperatures examined, which extended up to 445°.

The solubility of hydrogen in solid palladium at pressures up to

1 atm had previously been extended to 1123° by Sieverts (1914) who found that up to this temperature solubilities (compared at the same temperature) continued to exhibit a gradual decrease; and further estimates at still higher temperatures (see Sieverts, 1929; cf Smith,

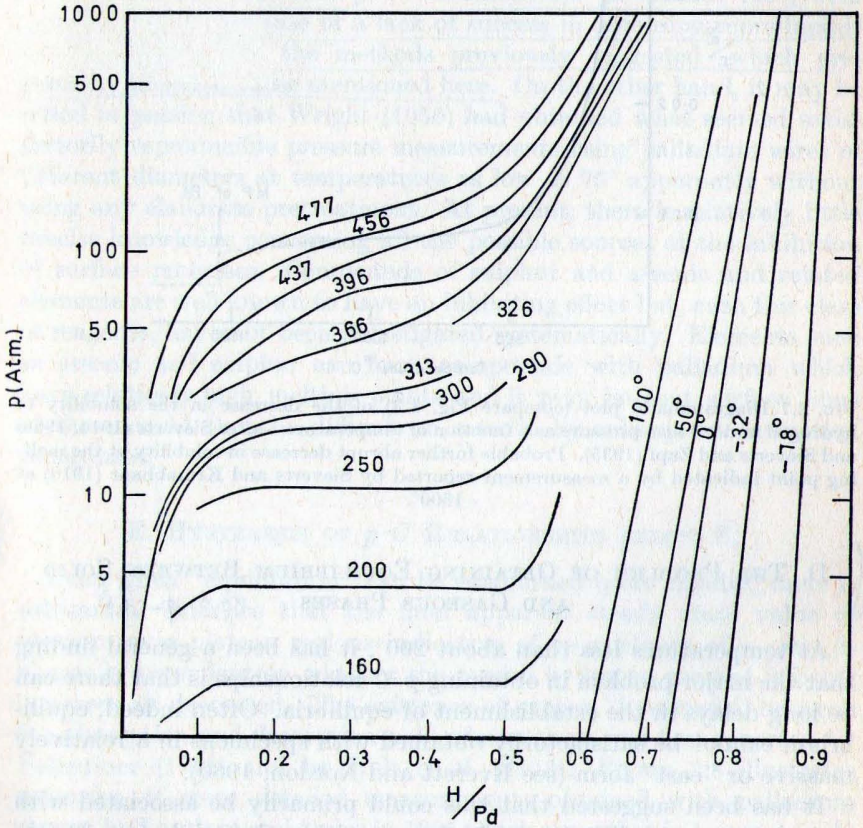


FIG. 2.6 Plots of p–C relationships at higher temperatures and pressures after Levine and Weale (1960), comparing their own results with those of Gillespie *et al.* (1926, 1936) and Perminov *et al.* (1952).

1948) suggest that this trend continues up to the melting point of palladium ($\sim$1550°) where it may be inferred (from a measurement of solubility in liquid palladium at 1600° reported by Sieverts and Krumbhaar, 1910) that there is a further discontinuous abrupt decrease (Fig. 2.7).

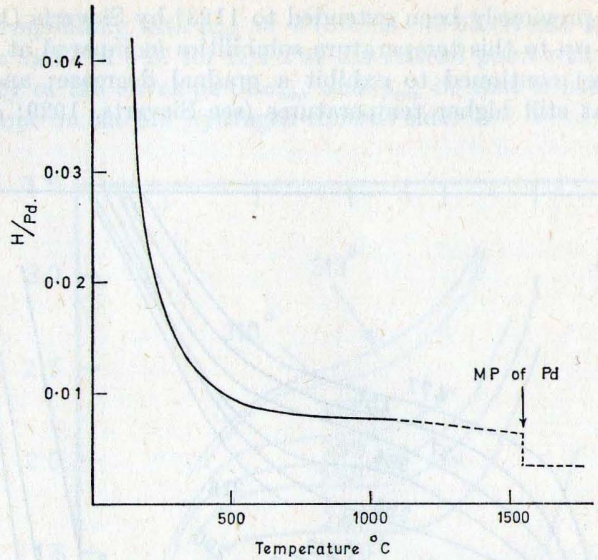


FIG. 2.7 Diagrammatic plot (compare Fig. 1.3) of the decrease in the solubility of hydrogen under 1 atm pressure as a function of temperature—after Sieverts (1914, 1929) and Sieverts and Zapf (1935). Probable further abrupt decrease in solubility at the melting point indicated by a measurement reported by Sieverts and Krumbhaar (1910) at 1600°.

D. The Problem of Obtaining Equilibrium Between Solid and Gaseous Phases

vor p 78

At temperatures less than about 200°, it has been a general finding that the major problem in obtaining p–C relationships is that there can be long delays in the establishment of equilibria. Often indeed, equilibrium cannot be satisfactorily obtained with specimens in a relatively massive or "cast" form (see Everett and Nordon, 1960).

It has been suggested that this could primarily be associated with slow processes of diffusion of hydrogen within the solids (see Smith, 1948). Currently, however, (Tiedema *et al.*, 1959) the evidence indicates that where equilibria is only slowly attained or where its establishment is virtually inhibited, this is usually due to the surface being relatively inactive catalytically for the processes of dissociation and recombination of hydrogen molecules. Pretreatment procedures have been used in order to activate the surface. Krause and Kahlenberg (1935) substantially increased the surface activity of their foils for absorption of hydrogen at 30° by previously electrolytically charging their specimens several times, in between which the hydrogen was rapidly expelled by

heating to a substantially higher temperature. The method of bombardment by ions of argon during low pressure gas discharges has been employed with some success by Ulbrich (1939), Norberg (1952) and by Jewett and Makrides (1965).

Nevertheless, Everett and Nordon (1960) have quite recently stated that they had to abandon p–C measurements (at around 120°) with palladium wires because of a lack of success in obtaining reproducible results with any of the methods previously suggested—which presumably included those mentioned here. On the other hand, it may be noted in passing that Wright (1950) had obtained what seemed satisfactorily reproducible pressure measurements using palladium wires of different diameters at temperatures as low as 75° apparently without using any elaborate pretreatment. At present, there is relatively little precise knowledge concerning all the possible sources of the inhibition of surface processes. Compounds of sulphur and arsenic and related elements are well known to have an inhibiting effect but, even this class of reagents, have not been investigated systematically. Elements such as arsenic and sulphur can form compounds with palladium which have relatively high melting points and it may be that surface films of these could then be difficult to remove by subsequent activation procedures.

E. Hysteresis of p–C Relationships below T_c

Even when "equilibrium" can be established quite rapidly, there is substantial evidence that the final apparent steady state value of pressure over plateau regions indicative of co-existence of α- and β-phases is dependent on whether the overall hydrogen content is being increased or decreased. The existence of such a "hysteresis" between the absorption and desorption p–C relationships was first reported by Valentiner (1911) and by Holt *et al.* (1913). Figure 2.8 illustrates examples of more detailed measurements obtained with palladium sponge by Lambert and Gates in 1925 which show that in a repeat cycle of measurements, the pressures over the absorption branch of the plateau region were only slightly reduced; and that the pressures in the desorption branch were almost precisely repeated.

It has been quite widely held that hysteresis merely reflects a failure to establish true equilibrium. This was the view of Gillespie and Hall (1926); and in determining p–C relationships over a temperature range from 0 to 180°, they claimed to have been able to obtain equilibrium by always heating the specimens to 360° before each measurement. Since then, however, their contention has been disputed in the light of an

increasing body of opposed evidence obtained in other studies in which measurements were made entirely isothermally.

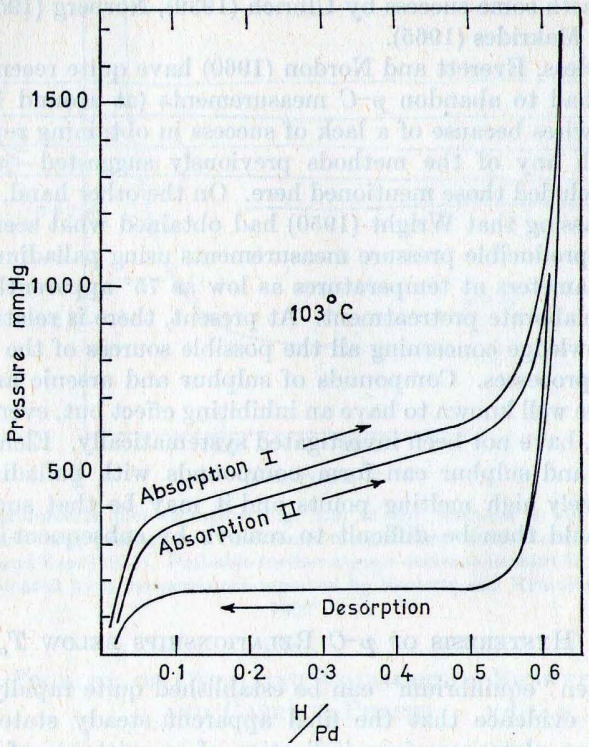


FIG. 2.8 Examples of hysteresis loops obtained with palladium sponge—after Lambert and Gates (1925).

In what was chronologically the next substantial investigation, hysteresis loops of considerable extent were observed by Brüning and Sieverts (1933) both with specimens in the form of wires at 160 and 200° and with finely divided blacks at 120 and 140°. The authors claimed that hysteresis was an inherent property of the system. Figure 2.9 is an amended reproduction of their plots of the logarithm of the pressure over the plateau regions which combines their own results with those of other authors as given in Table 2.1 and suggest that the absorption ($p_{\alpha,\beta}$) and desorption ($p_{\beta,\alpha}$) pressures fall on two separate lines which intersect at T_c. Brüning and Sieverts believed that the procedure employed by Gillespie and Hall would have yielded absorption relationships.

This view, however, is not very well supported by the fact that

Gillespie and Hall's values fall roughly midway between the absorption and desorption values of Brüning and Sieverts at temperatures of 160 and 180° where comparisons can be made directly (see Table 2.1). If

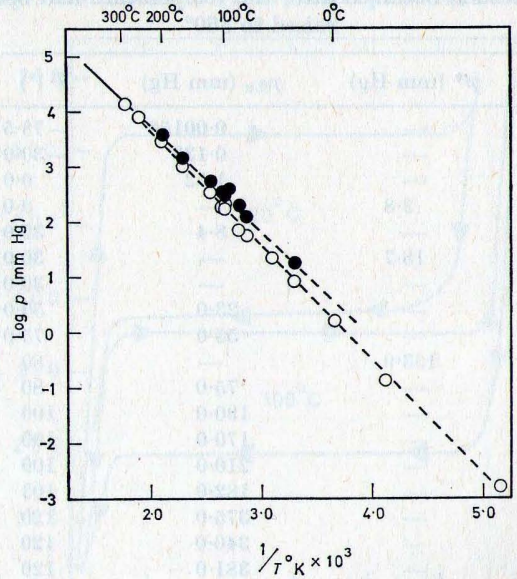


FIG. 2.9 Plots against $\frac{1}{T(^\circ K)}$ of values of $p_{\alpha,\beta}$ (filled symbols) and $p_{\beta,\alpha}$ (open symbols) given in Table 2.1—cf. Brüning and Sieverts (1933).

Gillespie and Hall's values really did fall at intermediate values this would support the findings of Bartsch (1911), an early collaborator of Sievert's, whose results were obtained with palladium blacks and only published as a thesis, but who reported that pressures over the plateau region at a temperature of ~120° during both absorption and desorption of hydrogen eventually could assume a mean value after prolonged standing.

Nevertheless, Bartsch's findings seem never to have been confirmed in any subsequent investigations including those by Sieverts with Brüning (1933) and Danz (1937) where very substantial hysteresis loops were recorded with palladium blacks at 80, 100, 120 and 140° (see Fig. 2.10).

Moreover, as indicated in Table 2.1, Danz's results are in keeping with the later findings of Wright (1950) of similar values of $p_{\alpha,\beta}$ and $p_{\beta,\alpha}$ during measurements of changes of equilibrium pressure (conjointly with electrical resistance—see Chapter 5) with wires of two different

TABLE 2.1

Vapour pressures at the beginning of regions of virtual potential invariance: p^* represents results obtained after the temperature had been temporarily raised to 360°

$p_{\alpha,\beta}$ (mm Hg)	p^* (mm Hg)	$p_{\beta,\alpha}$ (mm Hg)	T (°)	Reference
—	—	0·00156	−78·5	a
—	—	0·133	−30·0	a
—	—	1·52	0·0	a
—	3·8	—	0·0	b
—	—	8·4	30·0	a
—	18·7	—	30·0	b
17·35	—	—	30·0	c
—	—	23·0	50·0	a
128·0	—	55·0	75·0	d
—	153·0	—	80	b
200·0	—	75·0	80	e
350·0	—	190·0	100	e
310·0	—	170·0	100	d
340·0	—	210·0	100	f
357·0	—	182·0	103	g
620·0	—	375·0	120	e
520·0	—	340·0	120	h
631·0	—	381·0	120	i
669·0	—	980·0	140	i
1431·0	—	1034·0	160	i
1596·0	—	1026·0	160	j
—	1326·0	—	160	b
2529·0	—	1802·0	180	i
2538·0	—	1801·0	180	j
2639·0	—	1771·0	180	j
—	1960	—	180	b
3412·0	—	3002·0	200	k
3829·0	—	2960·0	200	i
3800·0	—	2948·0	200	j
4681·0	—	3519·0	210	j
4355·0	—	3283·0	210	j
6506·0	—	5175·0	230	j
6323·0	—	5077·0	230	j
8847·0	—	8389·0	250	j
11820·0	—	11500·0	270	j
14630·0	—	14440·0	290	j

(a) Wicke and Nernst (1964); (b) Gillespie and Hall (1926); (c) Nace and Aston (1957); (d) Wright (1950); (e) Sieverts and Danz (1937); (f) Owen and Jones (1937), Owen and Williams (1944); (g) Lambert and Gates (1925); (h) Everett and Nordon (1960); (i) Brüning and Sieverts (1933)-black; (j) Brüning and Sieverts (1933)-wire; (k) Gillespie and Galstaun (1936).

diameters. Furthermore, both sets of measurements also fall within the ranges of values quoted for the pressures recorded over regions of α- and β-phase co-existence during both absorption and desorption of hydrogen, respectively, by Owen and Jones (1937), and by Owen and Williams (1944)

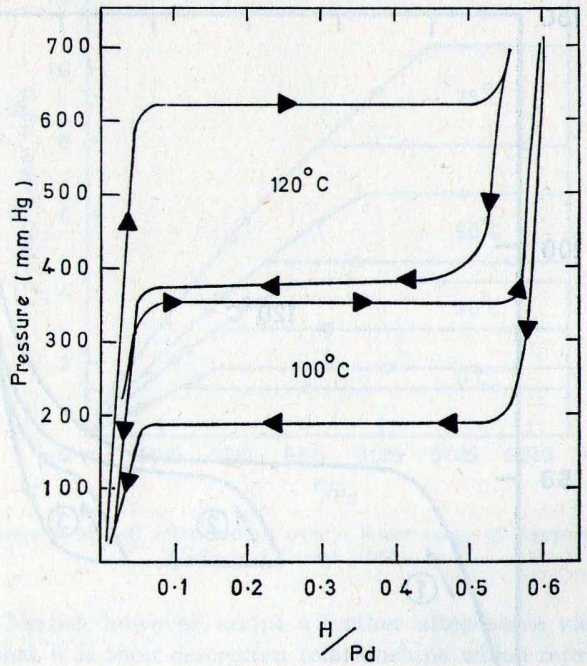


FIG. 2.10 Hysteresis of p–C isotherms obtained with palladium blacks—after Sieverts and Danz (1937).

(see also Owen, 1944) which were recorded in conjunction with measurements of changes of lattice parameters—see also Chapter 9. Incidentally, Gillespie also tacitly admitted the existence of hysteresis in his paper with Galstaun (1939) in which the heat treatment technique was not employed. Unfortunately, the lowest temperature in this study was 200°—so that there was no overlap with Hall's measurements which only extended to 180°.

More recently, Everett and Norden (1960) have broadly confirmed Lambert and Gates' (1925) findings (curiously enough with the same batch of palladium sponge) of the repeated tracing out of the same loop in successive cycles of absorption and desorption at 120° as shown in Fig. 2.11. This has led them to an independent restatement of much of Brüning and Sieverts' earlier arguments; and they have similarly

suggested that Gillespie and Hall's measurements really corresponded to "absorption" relationships. Some measurements at 30° reported by Nace and Aston (1957) also seem generally in keeping with this view since their values of p ($\sim$18 mm Hg) recorded over regions of constant

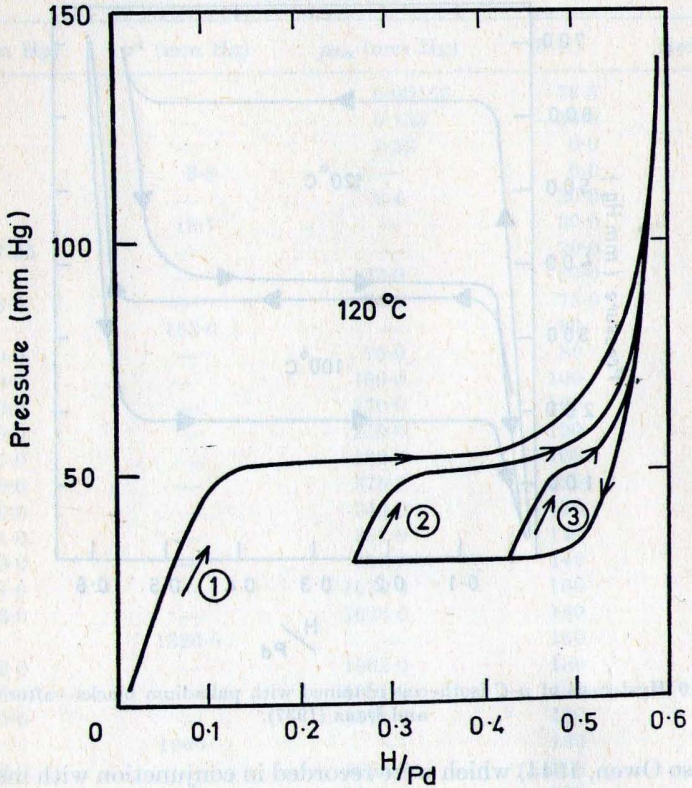


FIG. 2.11 Hysteresis of p–C relationships in cycles of absorption and desorption—after Everett and Nordon (1960).

pressure during *isothermal* absorption measurements with palladium blacks were in quite good agreement with the so-termed equilibrium values of Gillespie and Hall at 30°. Nace and Aston, however, concluded that their isotherm also corresponded to true equilibrium conditions, although hysteresis seemed to be indicated by the pressure reducing, during desorption, to virtually time-invariant values of $\sim$7 mm Hg at quite high hydrogen contents where α- and β-phase hydrides must still have co-existed within the specimens.

This likelihood seems to be borne out by the fact that marked

hysteresis has been recorded in the most recently derived series of p–C relationships of Wicke and Nernst (1964) obtained with palladium blacks at a series of temperatures from −78·5 to 75° (see Fig. 2.12).

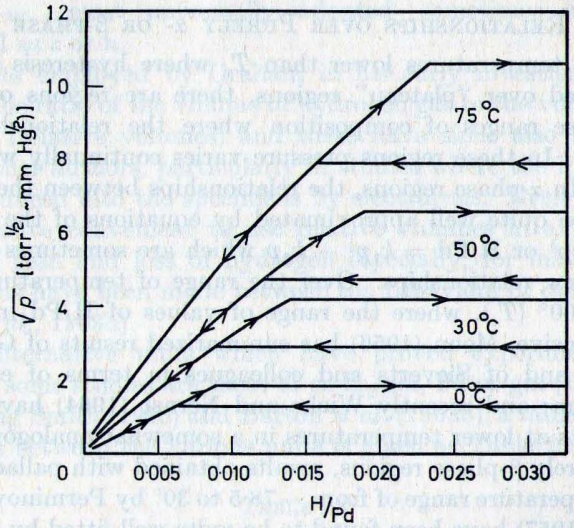


FIG. 2.12 Hysteresis of p–C relationships over a lower range of temperatures—after Wicke and Nernst (1964).

Wicke and Nernst, however, adopt a further alternative viewpoint in the claim that it is their *desorption* relationships which represent true thermodynamic equilibrium conditions.

It may be noted in passing that it has been pointed out by Libowitz (1958) that an apparent gradual increase of the steady-state pressure over regions of α- and β-phase co-existence could alternatively occur if the entire specimen is not maintained uniformly at the desired temperature.

A number of alternative explanations of hysteresis phenomena have been proposed (Smith, 1948). Latterly, most attention has centred around the possibility that hysteresis is a reflection of differences in the states of strain of the lattice during expansion in the formation of the β- from the α-phase, and contraction during the β- → α-phase transformation, respectively. Comparisons have been drawn with hysteresis effects over the whole field of nucleation phenomena and particular factors which have been discussed or considered are types and distribution of defects and the effect of crystallite size which may have a bearing on the extent of the hysteresis loop and on whether the equilibrium

pressure will or will not remain constant over the whole range of hydrogen contents of the phase transformations (Ubbelohde, 1937; Wagner, 1944; Everett and Nordon, 1960; Scholtus and Hall, 1963).

F. p–C Relationships over Purely α- or β-phase Regions

Even at temperatures lower than T_c where hysteresis effects may be exhibited over "plateau" regions, there are regions of purely α- and β-phase ranges of composition where the relationships remain coincident. In these regions pressure varies continually with changes of H/Pd. In α-phase regions, the relationships between them has been found to be quite well approximated by equations of the form H/Pd (or C) $= kp^{\frac{1}{2}}$ or H/Pd $= k_1p^{\frac{1}{2}} + k_2p$ which are sometimes termed the Sieverts Law relationships. Over the range of temperatures between 160 and 300° (T_c), where the range of values of H/Pd in α-phase is fairly extensive, Moon (1956) has summarized results of Gillespie and colleagues and of Sieverts and colleagues in terms of equations of similar form; and recently Wicke and Nernst (1964) have expressed their results at lower temperatures in a somewhat analogous way.

Over purely β-phase regions, results obtained with palladium blacks over a temperature range of from −78·5 to 30° by Perminov, Orlov and Frumkin (1957) have been found to be quite well fitted by an equation of the form H/Pd $= a + b \log p$ up to pressures of ~1000 atm (Fig. 2.6). These results have more recently been broadly confirmed by Wicke and Nernst (1964) (Fig. 2.4) over lower values of this range of pressures and over approximately the same range of temperatures.

G. Relationships at Very Low Temperatures

Below −78·5° the only measurements of equilibrium pressure as a function of hydrogen content have been obtained by Suhrmann *et al.* (1959, 1964) with evaporated palladium films at −196°. These indicated that the equilibrium pressure over an analogous plateau region had fallen to $\sim 10^{-4}$ mm Hg. However, the maximum hydrogen content corresponding to this constant pressure region seemed to have increased to a value approximating to PdH_2. There seems a possibility that this estimate may be too high since Suhrmann *et al.* (1959) also found the analogous content in similar experiments at −78·5° to be almost equally high, whereas Wicke and Nernst (1964) found H/Pd at β_{min} to be about only half of this ratio in their experiments with finely divided blacks and, as discussed above, their rather more comprehensive measurements form part of a consistent gradual trend from higher temperatures.

H. Units of Composition

So far hydrogen content has been generally expressed as the atomic ratio (H/Pd) which was employed as early as 1895 by Hoitsema and currently is almost universally adopted—sometimes alternatively symbolized as c or n.

The units employed by Graham in his early investigations were, however, the ratio of the volume of hydrogen gas to the volume of solid palladium (relative volumes) and these have since also been widely used by other authors, particularly in studies where the hydrogen has been introduced into the specimens by electrolysis. Even currently it can still prove convenient to use relative volumes in expressing the *kinetics* of gain and loss of hydrogen especially, for instance, where comparisons have been made between the behaviour of different alloys (Barton *et al.*, 1963b).

Other alternative units which have proved experimentally convenient in some studies are those of cc H_2/gm, Pd or gm (H_2)/gm (Pd).

Following Smith (1948) and Barton *et al.* (1963b), a table of conversion factors between the various units is given as Table 2.2.

Table 2.2

Interconversion of measures of hydrogen content[1]

	H/Pd ×	Relative volumes ×	$mgH_2/100g$ ×	ccH_2/gPd ×
H/Pd	—	$\sim 7{\cdot}9 \times 10^{-4}$	$1{\cdot}06 \times 10^{-3}$	$\sim 9{\cdot}5 \times 10^{-3}$
Relative volumes ($ccH_2/ccPd$)	$\sim 1{\cdot}25 \times 10^{3}$	—	~1·33	~12·0
$mgH_2/100gPd$	$\sim 9{\cdot}40 \times 10^{2}$	$\sim 7{\cdot}5 \times 10^{-1}$	—	~8·9
ccH_2/gPd	$\sim 1{\cdot}05 \times 10^{2}$	$\sim 8{\cdot}3 \times 10^{-2}$	$\sim 1{\cdot}11 \times 10^{-1}$	—

[1] Smith (1948), Barton *et al.* (1963b).

I. Relationships Between Electrode Potential and Hydrogen Content and Correlations with p–C–T Relationships

As stated in Chapter 1, electrolysis was employed as a method of introducing hydrogen into palladium by Thomas Graham in his early studies, and since then has been frequently used for this purpose. Until recently however, electrode potential measurements were only rarely carried out in conjunction. Indeed over the course of the last decade

the form of the relationships between electrode potential and hydrogen content has been the subject of some controversy and a number of publications have appeared concerning this. The more important difference of general principle now, however, seems to have been adequately resolved. A number of review articles concerning certain aspects have been published (Lewis, 1960, 1961a, 1962b; Barton and Lewis, 1963; Ives and Janz, 1961).

It is now generally accepted that there is an interdependence of the relationships between electrode potential and hydrogen content and the p–C–T relationships through the partial molar free energy for absorption of hydrogen.

The existence of this interrelationship seems to have been appre-

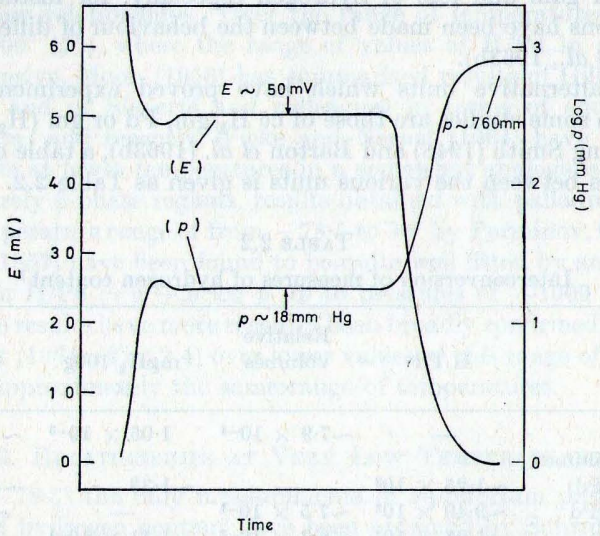


FIG. 2.13 Diagrammatic plots of changes with time in hydrogen-saturated solutions at *ca* 25° of the electrode potential and corresponding hydride vapour pressure of catalytically active palladium electrodes. Time to attain equilibrium ($E = 0$) is *ca* 2 hr with ·012 cm diam. wire specimens and *ca* 7 hr with ·027 cm diam. wire.

ciated in the 1930s by Nylén (1937) and also by Kandler and Knorr although these latter authors' findings were only reported somewhat later in the open literature (Breiter *et al.*, 1954). Both Nylén, in experiments during desorption of hydrogen, and Kandler, during absorption, found that the electrode potential altered with time during changes of hydrogen content in a similar manner to that shown in Fig. 2.13. Moreover, in both investigations the shape of the curves was interpreted as reflecting changes of H/Pd through the α-phase ranges of

composition, the α- → β-phase transformation, and through β-phase ranges of composition, respectively—this sequence, of course, being reversed when hydrogen is being continually desorbed. More recently these general conclusions have been confirmed in studies where the actual changes of hydrogen content has been derived from concurrent measurements of changes of other properties such as electrical resistance (Flanagan and Lewis, 1959) or X-ray lattice parameters (Aben and Burgers, 1962).

A schematic plot indicating the form of the relationships at *ca* 25° between electrode potential and hydrogen content which has been derived from such measurement is shown in Fig. 2.14. There is general evidence from the results of several investigators for the hysteresis of the relationships over regions of α- and β-phase co-existence (Ratchford and Castellan, 1958; Barton and Lewis, 1963). This appears to lend

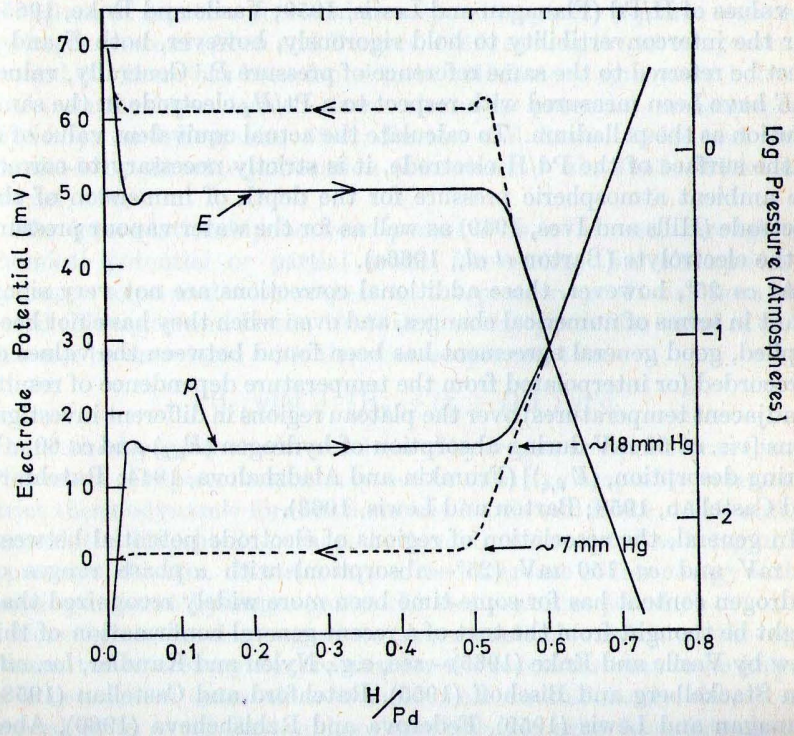


FIG. 2.14 Diagrammatic plots of relationships at *ca* 25° during both absorption and desorption of hydrogen, between hydrogen content and electrode potential measured w.r.t. a Pt/H_2 electrode in the same solution—see Frumkin and Aladzhalova (1944), Barton and Lewis (1963)—and equivalent derived p–C relationships.

some further support to the view that a hysteresis of the p–C relationships below T_c is an inherent property of the system. Experimental observations which seem to have a bearing on explanations of hysteresis in terms of lattice strains are that the E against time curves can exhibit what have been termed "supersaturation minima" (Ratchford and Castellan, 1958; Flanagan and Lewis, 1959; Hoare, 1960a) and "subsaturation maxima" (Green and Lewis, 1966b) at the beginning of the plateau regions over which the greater part of the α- → β- and β- → α-phase transformations are occurring. [Recent evidence of A. J. Maeland and T. B. Flanagan (private communication) suggests, however, that in several instances, such effects may have been artifacts resulting from sluggishness in the complete hydrogen-saturation of the solution around the Pt/H_2 reference electrode].

Calculations have shown that values of E can be almost exactly interconvertible with p through the relationship $2FE = RT \ln p/P$ for all values of H/Pd (Flanagan and Lewis, 1959; Vasile and Enke, 1965). For the interconvertibility to hold rigorously, however, both E and p must be referred to the same reference of pressure P. Generally, values of E have been measured with respect to a Pt/H_2 electrode in the same solution as the palladium. To calculate the actual equivalent value of P at the surface of the Pd/H electrode, it is strictly necessary to correct the ambient atmospheric pressure for the depth of immersion of the electrode (Hills and Ives, 1949) as well as for the water vapour pressure of the electrolyte (Barton *et al.*, 1966a).

At *ca* 25°, however, these additional corrections are not very significant in terms of numerical changes, and even when they have not been applied, good general agreement has been found between the values of E recorded (or interpolated from the temperature dependence of results at adjacent temperatures) over the plateau regions in different investigations [*viz. ca* 50 mV during absorption of hydrogen ($E_{\alpha,\beta}$) and *ca* 60 mV during desorption, ($E_{\beta,\alpha}$)] (Frumkin and Aladzhalova, 1944; Ratchford and Castellan, 1958; Barton and Lewis, 1963).

In general, the association of regions of electrode potential between 50 mV and *ca* 150 mV (25°—absorption) with α-phase ranges of hydrogen content has for some time been more widely recognized than might be thought from the text of a recent general confirmation of this view by Vasile and Enke (1965)—see, e.g., Nylén and Kandler, *loc. cit.*, von Stackelberg and Bischoff (1955), Ratchford and Castellan (1958), Flanagan and Lewis (1959), Federova and Rzhishcheva (1960), Aben and Burgers (1962). Recently this has been fully confirmed by a detailed study of Simons and Flanagan (1965a) who have obtained close agreement between p–C relationships which they have derived over this and

analogous regions over a range of temperatures from 0–90°, and p–C relationships in α-phase derived by direct equilibration by Wicke and Nernst (1964) at temperatures which overlap this range.

Another important consideration concerning the derivation of p–C relationships from electrode potential measurements has been brought out by Simons and Flanagan in their studies in which the hydrogen content of the specimens was increased by spontaneous absorption of hydrogen gas dissolved in the solution. The rate of absorption must not be so rapid compared with internal equilibration by diffusion (see also Chapter 7) that an appreciable concentration gradient can exist through the specimen. Simons and Flanagan have reduced this source of error to a minimum by using rather slow rates of absorption by lowering the partial pressures of hydrogen in their solutions by dilution with an inert gas.

The regions of Fig. 2.14 between 50 mV and zero and then extending to regions of negative potential correspond to purely β-phase regions of hydrogen content (Aben and Burgers, 1962) and, again, at temperatures around 25° there has been found to be satisfactory agreement between p–C relationships derived from electrode potential measurements (Federova and Frumkin, 1953; Barton and Lewis, 1963) and those obtained by direct equilibration (Perminov *et al.*, 1957; Wicke and Nernst, 1964).

The interrelationship between p and E is, of course, through the chemical potential or partial molar free energy for absorption of hydrogen expressed with respect to the pressure p. It has been proposed (Flanagan and Lewis, 1959) that at any particular value of H/Pd this can be associated with the microscopic reaction.

$$x\mathrm{H} : y\mathrm{Pd} + \tfrac{1}{2}\mathrm{H}_2 \rightarrow (x+1)\mathrm{H} : y\mathrm{Pd}$$

where x and y are the total numbers of hydrogen and palladium atoms. This mode of representation may not be entirely acceptable in terms of strict thermodynamic formulations (see Vasile and Enke, 1965) and, in general, the $\frac{1}{2}H_2$ should perhaps be formally subscripted as being under a pressure of 1 atm. In strict terms, the difference in free energy is that existing between hydrogen gas at the two pressures p and P.

Nonetheless, having regard to the non-stoichiometry of the solid phases, the microscopic expression for the reaction seems to be helpful in a descriptive sense since it is at least so sufficiently simple and general as to avoid the ambiguities which can arise from introducing correlations of the content with particular α- or β-phase compositions or symbolism, or with also possibly misleading introduction of stoichiometric formulae such as Pd_2H (Nace and Aston, 1957).

J. Catalytic Activity of Electrodes and the Interconversion of E and p

Because of the stubborn retention of presorbed films of impurities or else as the result of the adsorption of chemical poisons from the solution, the apparent electrode potentials can differ widely from values that can be correlated with p in the sense discussed above (see Flanagan and Lewis, 1959). Alternatively, a partially deactivated state may occur in which the electrode may not adopt obviously erroneous values but may be rather slow to equilibrate with hydrogen molecules dissolved in solution. This latter condition seems likely to have been at the root of the apparent discrepancies which have given rise to such disputes concerning relationships between electrode potential and hydrogen content as have occurred over the last decade (see Federova and Rzhishcheva, 1960). At present it seems possible that unambiguous measurements of electrode potential from the point of interconvertibility with p–C relationships have been obtained only with specimens which measurements of the pressure and temperature dependence of rates of absorption and desorption of hydrogen molecules dissolved in solution have indicated to be sufficiently catalytically active for the kinetics to be governed by transport of the hydrogen through the Brunner–Nernst boundary layer of solution adjacent to the surface of the electrode (Fallon and Castellan, 1960; Carson *et al.*, 1960; Flanagan and Lewis, 1961b; Barton *et al.*, 1963b). Electrodes with such a sufficiently high activity have been prepared by prior oxidation of the surface by either heating in oxygen (Simons and Flanagan, 1965) or electrolytic anodization (Clamroth and Knorr, 1953; Flanagan and Lewis, 1959). Alternatively an active surface can be attained by electroplating on a further thin layer of palladium black (palladization) (Flanagan and Lewis, 1959; Barton *et al.*, 1963b).

K. Independence of the E Against H/Pd Relationships on the Methods of Introducing or Removing Hydrogen

Provided the electrode has a high catalytic activity for equilibrating with molecular hydrogen, the general form of the E against H/Pd relationships has been found (Flanagan and Lewis, 1959) to be independent of whether the hydrogen is being absorbed (or desorbed) by means of either electrolytic methods or in the course of spontaneous equilibration with molecular hydrogen dissolved in solution. Once again, these methods are to be employed with the proviso that the rates of absorption (or desorption) are not so fast as to give rise to such a high

concentration gradient within the specimen that the surface layers have a possibly misleadingly high (or low) hydrogen content in terms of the overall hydrogen content of the specimen (Flanagan and Lewis, 1959; Barton *et al.*, 1963b).

The rate of absorption of dissolved hydrogen from solution can be expressed as $k_0(P-p)$ under conditions where transport of the dissolved molecules up to the surface of the electrode is the slow kinetic step—where P is the pressure under which the hydrogen is dissolved in solution, and p is the vapour pressure of the hydride which can be derived from E.

When initially hydrogen-free specimens are immersed in solutions saturated with hydrogen at roughly atmospheric pressure, the rate of absorption when p is small compared to P, is approximately equal to k_0 which (in vigorously stirred solutions) has a value of $\sim 10^{16}$ molecules cm^{-2} sec^{-1} (atm^{-1}) (see Barton and Lewis, 1962b). By comparison, approximately the same rate of absorption could be effected by cathodization at current densities of $\sim$3mA cm^{-2}.

In the case of specimens equilibrating with hydrogen dissolved in solution, the value of p will complementarily increase when E decreases (w.r.t. Pt/H_2) as absorption proceeds. This accounts for the exponential form of the E against time curve as $E \rightarrow 0$ in Fig. 2.13, as compared with the virtually linear relationship between E and H/Pd near $E = 0$ (Fig. 2.14).

L. The Palladium Bielectrode

Largely because of the rapid rate at which hydrogen can diffuse through palladium (see Chapter 7) there have been a number of experimental studies in which the palladium has been in the form of a membrane or septum which either separates two solutions—when it can be termed a bielectrode—or separates gaseous hydrogen on one side from a solution on the other. This latter arrangement has been made practical use of, both as a means for obtaining ultrapure hydrogen by electrolysis and in certain forms of fuel cells (see Chapter 7).

The bielectrode has been utilized in studies of hydrogen overpotential (see Frumkin and Aladzhalova, 1944; Trusov and Aladzhalova, 1960a) since the component of overpotential corresponding with the hydrogen content of the electrode can be measured during electrolysis on the side of the electrode remote from where hydrogen is being discharged electrolytically as indicated diagrammatically in Fig. 2.15. Problems of activating either side are similar to those discussed previously for more conventional forms. Different methods of sealing the electrodes into

surrounding materials have been proposed to avoid cracking due to stresses arising from expansion of the electrode during absorption of hydrogen (Barton and Lewis, 1961).

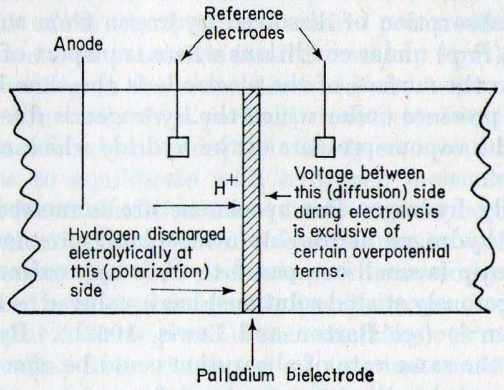


FIG. 2.15 Diagram of palladium bielectrode dividing two solutions—see Frumkin and Aladzhalova (1944), Trusov and Aladzhalova (1960a).

M. Other Measurements of Hydrogen Overpotential at Palladium Cathodes

Even at other forms of palladium cathodes such as wires, the component of hydrogen overpotential which can be correlated with hydrogen content in terms of p–C relationships can be conveniently obtained (compared with other metals such as platinum) by extrapolation back to zero time of plots against time of functions of the open circuit measurements of electrode potential made after interruption of cathodization (Clamroth and Knorr, 1953; Barton and Lewis, 1962b; Green and Lewis, 1964). This is largely because the open circuit potential changes slowly because of the "sink" of hydrogen introduced during electrolysis.

A further feature of overpotential measurements with palladium cathodes is that under conditions where transport of hydrogen molecules through the Brunner–Nernst layer controls the absorption of hydrogen, the rate constant k_0 can be measured prior to electrolysis from, for example, measurements of changes of electrical resistance (Barton and Lewis, 1962b). If transport control continues to be the slow step in the evolution of hydrogen during electrolysis, it is then possible to calculate the expected additional increase of the hydride or diffusion component of overpotential η_2 as a function of current density,

and then to compare these calculations with the experimental measurements (Kandler *et al.*, 1937; Barton and Lewis, 1962b; Green and Lewis, 1964; Hull and Lewis, 1965). These and related measurements have also been useful for estimating the upper limit of hydrogen content which can be introduced into palladium cathodes during electrolysis (Green and Lewis, 1964, 1966a)—see Fig. 2.16.

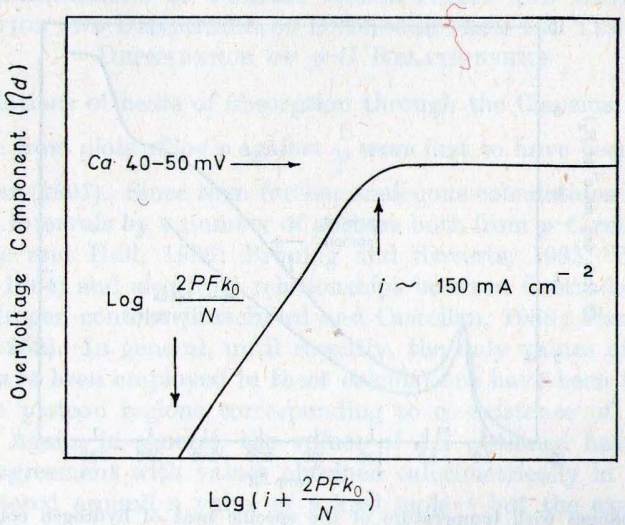


FIG. 2.16 Relationships in hydrogen-saturated solutions between the hydride or diffusion component of overpotential, η_d, and a logarithmic function of current density, i, and the rate constant, k_0, for diffusion of hydrogen molecules to a catalytically active electrode surface—indicating the attainment of a limiting value of η_d with the onset of the evolution of hydrogen bubbles.

N. Calorimetric Determinations of Heats of Absorption and Desorption of Hydrogen and of the Specific Heat of Hydrogen in Palladium

Calorimetric measurements of heats of absorption of hydrogen by finely divided palladium powders ("blacks") have been in general agreement in suggesting a value of ~9kcal mole^{-1} H_2 (Favre, 1873; Mond *et al.*, 1895; Gillespie and Ambrose, 1931).

Aston and his colleagues have also obtained values of a similar order of magnitude in the most recent series of calorimetric studies in which measurements have been made of both heats of absorption as well as of specific heats.

The specific heat measurements have been made with specimens in the form of a framework constructed from 1 mm thick discs of palladium

(Mitacek and Aston, 1961, 1963; Aston and Mitacek, 1963) as well as in the form of blacks (Nace and Aston, 1957; also Mackliet and Schindler, 1966). Both types of samples yielded broadly similar results but the values of Cp with the blacks were generally significantly higher—the difference increasing somewhat with increasing temperature as indicated in Fig. 2.17. The form of the λ-type specific heat anomaly with a

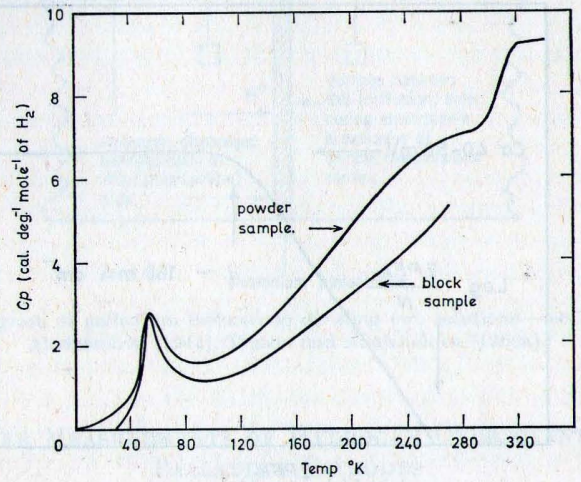


FIG. 2.17 Changes with temperature of the specific heat of hydrogen contained in samples of palladium for which H/Pd $\sim$ 0·50—after Nace and Aston (1957), Mitacek and Aston (1963).

maximum at *ca* 50° was found to be virtually independent of the hydrogen content within a range of H/Pd from 0·125 to 0·07. The shape and position of this anomaly as a function of temperature have been compared with the form of the rotational specific heat of equilibrium mixtures of ortho- and para-hydrogen Lewis (1962)—see also Chapter 10.

Measurements of heats of absorption of hydrogen have been recorded as a somewhat limited function of hydrogen content by Nace and Aston (1957) who obtained a fairly constant value of ~ -9600 cal mole^{-1} H_2 (30°). However, for one determination which extended over α-phase compositions ($0 <$ H/Pd $< \sim$0·104—mean value of H/Pd given as 0·052), a substantially lower (neglecting sign) value of -8948 cal was recorded. (Results indicated that the heats of absorption in the α-phase deuteride were also lower than over analogous regions of α- and β-phase co-existence—see Chapter 8.)

Nace and Aston also reported results for two determinations of the heat of *desorption* over which H/Pd corresponded to regions of α- and

β-phase co-existence, but they are somewhat ambiguous in that one result is somewhat higher (10280 cal). (Two analogous determinations of heats of desorption of deuterium from deuterided palladium were both lower than corresponding heats of absorption—see Chapter 8.)

O. Determinations of Partial Molar Heats and Entropies of Absorption and Desorption of Hydrogen from the Temperature Dependence of p–C Relationships

Calculations of heats of absorption through the Clausius Clapeyron equation from plots of log p against $\frac{1}{T}$ seem first to have been reported by Dewar (1897). Since then further analogous calculations have been made at intervals by a number of authors both from p–C relationships (Gillespie and Hall, 1926; Brüning and Sieverts, 1933; Wicke and Nernst, 1964) and also from relationships between electrode potential and hydrogen content (Ratchford and Castellan, 1958; Flanagan and Lewis, 1959). In general, until recently, the only values of p (or E) which have been employed in these calculations have been the values over the plateau regions corresponding to co-existence of α- and β-phases. Again, in general, the values of $\Delta\bar{H}$ obtained have been in overall agreement with values obtained calorimetrically in that they are scattered around a value of 9 kcal mole^{-1} but the exact values obtained are to some extent governed by factors such as the pre-treatment and the sequence in which the measurements are taken (see Nace and Aston, 1957) for reasons which still do not seem to have been fully resolved.

Corresponding partial molar entropy changes derived from the temperature dependence of the vapour pressure over regions of α- and β-phase co-existence have been found to have values ranging from about 22 to 24 cal mole^{-1} deg^{-1} (see Wicke and Nernst, 1964) which are again of the same order of magnitude as values calculated from a summation of the specific heat data obtained with palladium blacks (Nace and Aston, 1957). No results have been published of corresponding summations for the specific heat measurements recorded with more massive specimens by Mitacek and Aston (1963).

Quite recently heats of absorption of hydrogen in α-phase regions of hydrogen content have been calculated from the temperature dependence of plots against hydrogen content of $p^{\frac{1}{2}}$ or other functions which are more linear than p (Wicke and Nernst, 1964; Simons and Flanagan, 1965a; Brodowsky and Poeschel, 1965). Although no clearly perceptible differences of $\Delta\bar{H}$ as a function of hydrogen content have

been detected over these α-phase ranges, the average calculated values of $\Delta\bar{H}$ are perhaps even rather less than might have been suggested from trends in the calorimetric results (Nace and Aston, 1957, *loc. cit.*). They have been found to fall within a range from 4500 to 4780 cal mole^{-1} H_2, and thus are only about half values of $\Delta\bar{H}$ measured over regions of α- and β-phase co-existence.

CHAPTER 3

Changes of the Shape and of Mechanical and Elastic Properties of Palladium Resulting from Absorption and Desorption of Hydrogen

Perhaps the most unique feature of the formation of hydrides by palladium is the retention of substantial elasticity by the specimens. They can continue to stand up to quite rough handling without fracture and this can be of considerable practical advantage in making measurements of changes in physical properties as a detailed function of hydrogen content.

A. Changes of Elastic Constants as a Function of Hydrogen Content

Some preliminary measurements of changes of elastic constants with hydrogen content were made by Thomas Graham. Graham found a reduction of approximately 20% in the value of both Young's Modulus and of the breaking strain of specimens with hydrogen contents corresponding to values of H/Pd ~0·6—this has been broadly confirmed by the results of subsequent studies. In addition to making measurements of Young's Modulus, Koch (1917) and Lewis *et al.* (1953) also measured changes of Rigidity (Torsion) Modulus for β-phase hydrides and found this also to be reduced only by relatively small amounts with respect to pure palladium—about a 16% decrease being the highest figure obtained.

The most detailed studies of changes of Young's Modulus as a function of hydrogen content have been reported by Krüger and Jungnitz (1936) and extended to temperatures up to 224° by Jungnitz (1939). As in the experiments of Koch (1917), changes of hydrogen content were estimated from changes of electrical resistance and the stress was raised to sufficiently high values for measurements to have also been made of changes of the elastic limit and of the breaking strain. Results showed that at lower temperatures all three parameters show virtually no decrease at low contents of hydrogen, and indeed the

results of Krüger and Jungnitz at ambient room temperatures indicate that all three parameters pass through a maximum as indicated diagrammatically in Fig. 3.1. This finding seems to have been confirmed

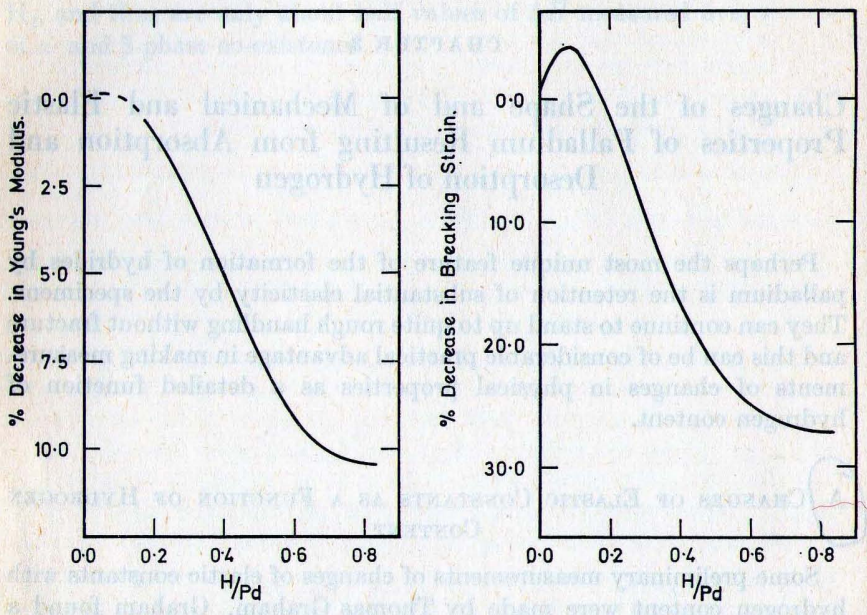


FIG. 3.1 Percentage changes of Young's Modulus and breaking strain as a function of hydrogen content at ambient room temperature as estimated from results of Krüger and Jungnitz (1936).

in some more recent measurements of stress–strain curves by Takagi and Sugeno (1965) which extended below room temperature.

B. Changes of Hardness and of Internal Friction

As compared with the changes of elastic constants, somewhat larger relative changes of the mechanical hardness and of internal friction can result from the absorption of hydrogen. On the other hand, however, changes of these parameters by a similar order of magnitude can also be effected by mechanical cold working of the palladium.

1. *Changes of Hardness*

Changes of hardness with hydrogen content were measured by Sugeno and Kowaka (1954). In these measurements the hydrogen was introduced by electrolysis; and although changes of hardness generally

were plotted by Sugeno and Kowaka as a function of the time of electrolysis, they could also be broadly correlated with changes of hydrogen content which were estimated concurrently by both differential coulometry and from changes of electrical resistance.

Figure 3.2 shows changes of hardness during the absorption of hydrogen by specimens which initially had hardnesses ranging from ~50 to ~110 on the Vicker's scale depending on the prior annealing procedure.

Results showed that for all specimens there was a marked increase of hardness with increasing hydrogen content over α-phase regions, which is in contrast to the comparatively small changes of elastic constants over the same range of composition. Moreover, there seems to be virtually no further increase of hardness with further increases of hydrogen content over regions of co-existence of α- and β-phases and of purely β-phase (Tiedema *et al.*, 1959). Indeed for specimens which initially had been heavily cold-drawn, Fig. 3.2 shows that there is a decrease of hardness when the hydrogen contents exceed α-phase concentrations. On subsequent removal of hydrogen from α-phase

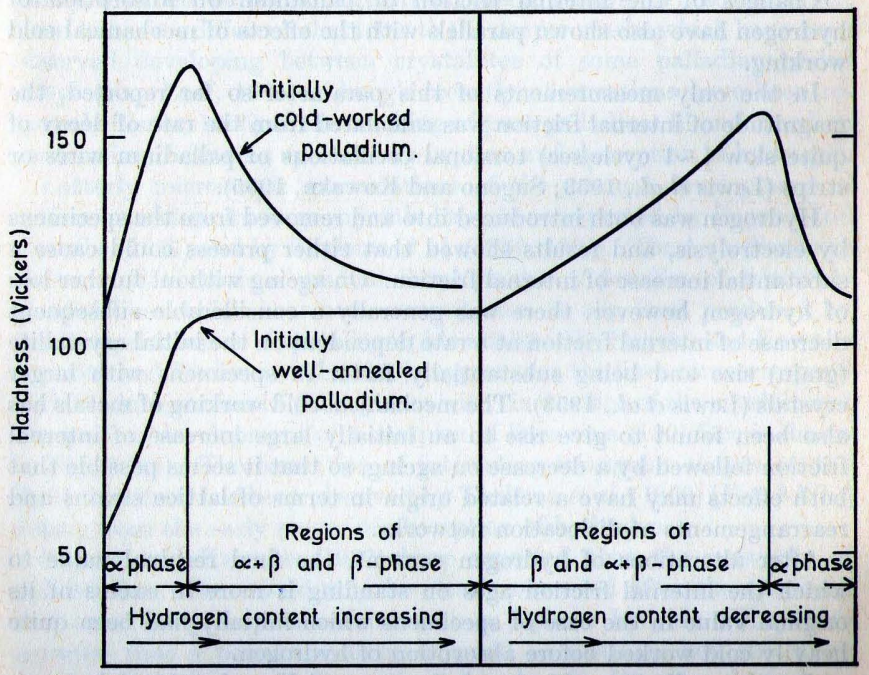


FIG. 3.2 Changes of hardness as a function of both introduction and subsequent removal of hydrogen by electrolysis at *ca* 25°—after Sugeno and Kowaka (1954).

hydrides, the hardness decreased back reversibly to not much greater than the original values.

It is also illustrated in Fig. 3.2 that on removal of hydrogen (either by anodic oxidation or by outgassing at 300°,) from β-phase hydrides, formed from initially fully annealed palladium, the course of changes is as follows. First there was a gradual increase of hardness which seemingly extended back up to and throughout the β- → α-phase transformation and over which evidence was obtained that its form was independent of the rate of removal of hydrogen. After this, there was a decrease over purely α-phase regions—although the final value when all the hydrogen had apparently been removed was still ~110 which was about double its initial hydrogen-free value. Furthermore, the annealing temperature (~450–600°) required to reduce the hardness to ~50 was the same as that required to similarly reduce the hardness of a mechanically cold-worked specimen.

2. *Changes of Internal Friction resulting from Absorption and Desorption of Hydrogen*

Changes of the internal friction of palladium on absorption of hydrogen have also shown parallels with the effects of mechanical cold working.

In the only measurements of this parameter so far reported, the magnitude of internal friction was calculated from the rate of decay of quite slow (~1 cycle/sec) torsional oscillations of palladium wires or strips (Lewis *et al.*, 1953; Sugeno and Kowaka, 1955).

Hydrogen was both introduced into and removed from the specimens by electrolysis, and results showed that either process could cause a substantial increase of internal friction. On ageing without further loss of hydrogen however, there was generally a considerable subsequent decrease of internal friction at a rate dependent on the initial crystallite (grain) size and being substantially faster in specimens with larger crystals (Lewis *et al.*, 1953). The mechanical cold working of metals has also been found to give rise to an initially large increase of internal friction followed by a decrease on ageing, so that it seems possible that both effects may have a related origin in terms of lattice strains and rearrangements of dislocation networks.

After alterations of hydrogen content, the final residual value to which the internal friction ages on standing is more in excess of its original value in the case of specimens which initially had been quite heavily cold worked before absorption of hydrogen.

As a lower limit to this trend, Sugeno and Kowaka (1955) have reported that where specimens contained large grains extending across

their width, the internal friction was hardly increased at all. However, this apparent lack of any increase in internal friction is in terms of comparison of values measured some 20 min after interruption of electrolysis—and the trends in measurements of the rates of decay of internal friction (Lewis *et al.*, *loc. cit.*) suggest that very large-grained specimens might show quite rapid decreases of internal friction prior to this. Unfortunately, with the methods of approach employed so far, it has proved difficult to make measurements of internal friction at very short times after electrolysis.

C. Microscopic Examination of Changes of the Topology of Palladium Surfaces Following Absorption of Hydrogen

There have been a number of reports of the microscopic observation of changes of the surfaces of palladium specimens following the absorption of hydrogen. For instance, Smith and Derge (1934), (also Smith, 1948) have shown the gradual development of at least partly oriented patterns of relatively deep gulleys. These, however, seem to have a different character to the deeper cracks which have been observed developing between crystallites of some palladium/nickel alloys (Van Loef, 1963) although recently observations have been reported (Eisner, 1965) of the cracking of pure palladium films formed on glass or iron following cycles of absorption and desorption of hydrogen.

Latterly microscopic examinations of the gradual development of surface markings on large crystals have been reported by Sugeno and Kawabe (1957) and by Tiedema *et al.* (1959, 1960). These studies have shown that there is a gradual development of families of relatively parallel lines which bear some resemblance to slip lines produced by mechanical stresses. Crystallographic analyses by Sugeno and Kawabe (*loc. cit.*) and Tiedema *et al.* (1959) suggest that the lines can correspond with the intersection of (111) planes with the surface of the crystal; and the gradual development of a complex of lines on a (100) face is shown in Fig. 3.3(a). The formation of interesting triangular shapes on the (111) face itself has been observed by Tiedema *et al.* (1960) [Fig. 3.3(b)] during even the early stages of absorption of hydrogen.

Sugeno and Kawabe (1957) have reported that the networks of parallel lines often could only be clearly observed after the specimen had been completely transformed to a β-phase hydride. They also reported that a pattern sometimes could be distinguished still more clearly after subsequent desorption of hydrogen either by electrolytic anodization or by heating at relatively low temperatures.

D. Changes of Shape of Palladium Specimens Following Repeated Cycles of Absorption and Desorption of Hydrogen

There can be considerable changes of the shape of palladium specimens after numerous cycles of absorption and desorption of hydrogen during which α- → β-phase and β- → α-phase transformations occur. In experiments of Loessner (1911) and of Krause and Kahlenberg (1935) with palladium sheets, the specimens have been shown to be substantially shortened and thickened to rather irregular shapes (see Fig. 3.4). Such deformations present problems in the use of palladium

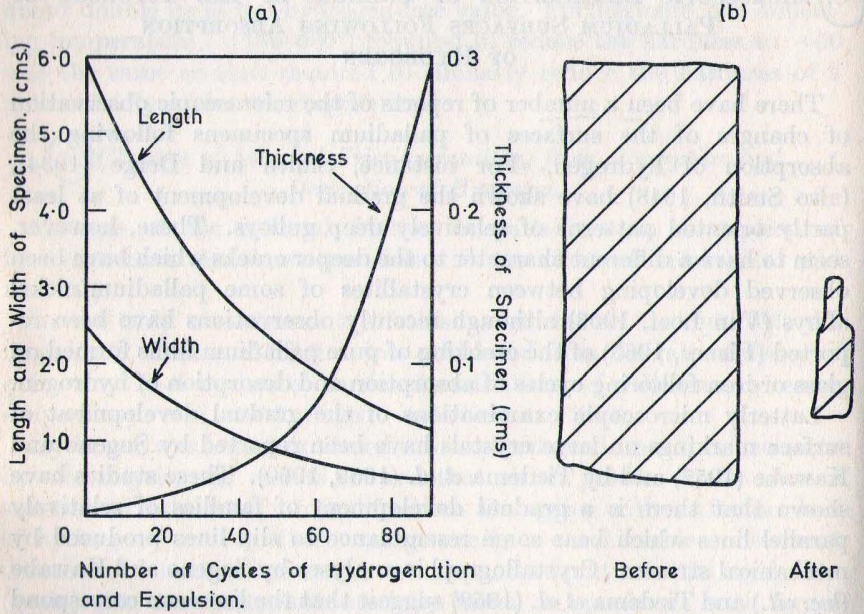
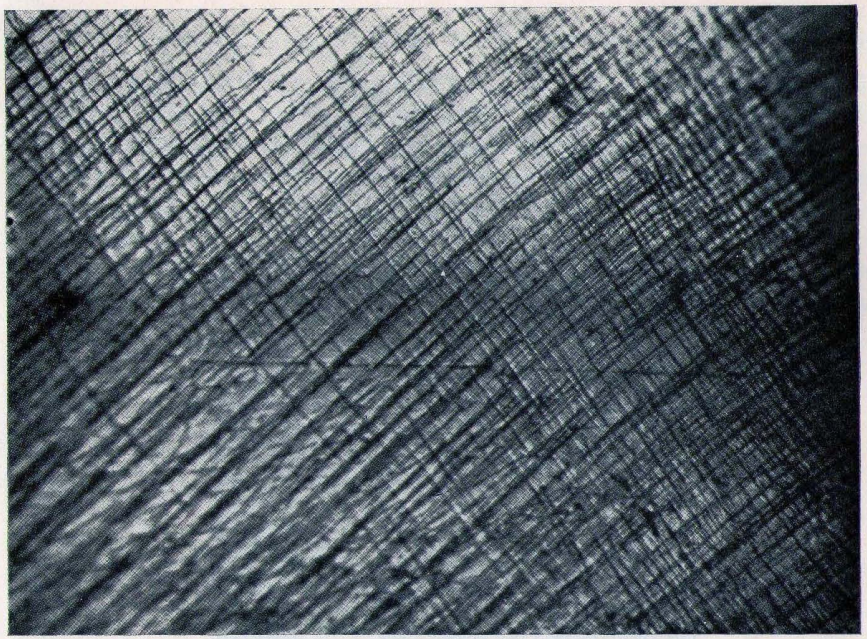


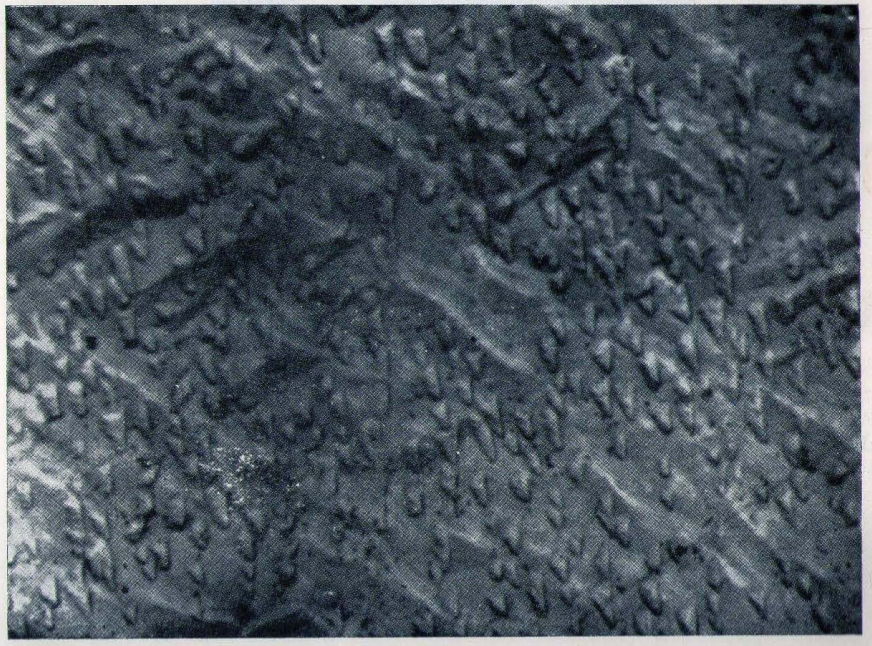
Fig. 3.4 (a) Decreases of the length and width, and complementary increases of the thickness, of a palladium sheet as a function of numbers of cycles of absorption of hydrogen by electrolysis followed by its expulsion by heating in a flame (b) Rough relative comparison of the appearance of the specimen in terms of length and width before and after 92 such cycles—after Krause and Kahlenberg (1935).

as diffusion membranes for hydrogen purification since cycles of phase transformations can occur if the specimen is repeatedly cooled down and reheated to a convenient working temperature in pressures of hydrogen which are commonly encountered.

This problem of deformation latterly has led to the widespread substitution for pure palladium of certain palladium alloys [particularly of



(a)



(b)

Fig. 3.3 (a) Families of slip lines developed on the (100) face of a palladium single crystal following the absorption of electrolytically discharged hydrogen (b) Triangular shapes developed on the (111) face of a palladium single crystal following the absorption of hydrogen. Reproduction by permission of Professor W. G. Burgers and Nederlands Akademie van Wetenschappen-Amsterdam.

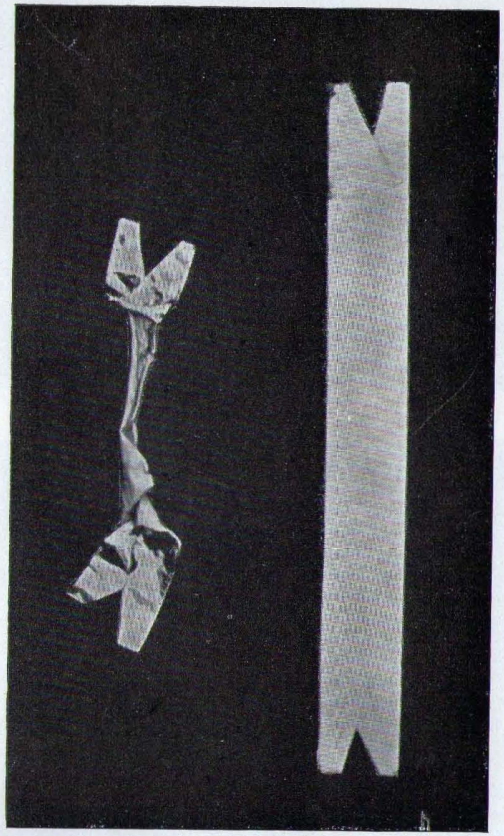


FIG. 3.5 Comparison of the appearance of specimens of pure palladium (left) and an alloy of palladium with ~25% silver (right) (initially the same size) after thirty cycles of heating and cooling in hydrogen gas at atmospheric pressure. Reproduced by permission of Dr. J. B. Hunter and Platinum Metals Review.

certain compositions in the palladium and silver series (Hunter, 1960; Connor, 1962 and Darling, 1963) which do not seem to undergo phase transformations within similar ranges of temperature and pressure and which can also permit even higher rates of permeation of hydrogen under comparable conditions as is further discussed in Chapter 7]. An illustration of the superior resistance to deformation of membranes of alloys containing 24–26% Ag is shown in Fig. 3.5. Latterly, further improvement in these alloys has been found if small amounts of boron are introduced into the Pd/Ag alloys (Küssner, 1965).

CHAPTER 4

Relationships between Hydrogen Content and Electrical Resistance

A. General Form of the Relationships Between H/Pd and R/R_0, and the Problem of Hysteresis

The first observations of the changes of electrical resistance with hydrogen content again were made by Thomas Graham (1869a) who reported that the resistance of specimens highly charged with hydrogen has increased by ~25%. Subsequently, measurements by Dewar (1878) and by Knott (1886) indicated that the increases of electrical resistance could be roughly in direct proportion to increases of hydrogen content over substantial ranges of H/Pd, but the first comprehensive attempts to correlate changes of electrical resistance with changes of hydrogen content seem to have been due to McElfresh (1904) and Fischer (1906). In Fischer's study (at 18°) the hydrogen was introduced by electrolysis and the increase of hydrogen content was estimated from the differences between the volume of hydrogen evolved concurrently at the palladium cathode and the volume of hydrogen evolved at the *platinum* cathode of a further cell which was connected in series. Sources of error in this experimental method to which attention was later drawn are: (1) the possibility of oxidizing products diffusing from the anode compartment and reducing some of the hydrogen (Rosenhall, 1935; Barton *et al.*, 1966a) and (2) the possibility of errors in the measurements of resistance resulting from co-conduction of the measuring current through the solution.

The changes of electrical resistance are generally expressed in terms of relative resistance R/R_0, where R is the actual resistance of the specimen and R_0 its initial resistance when free of hydrogen. As indicated in Fig. 4.1, the results derived by Fischer between R/R_0 and hydrogen content showed an almost linear increase over ranges of H/Pd corresponding to the α-phase region. At α_{max} (H/Pd ~0·015–0·025), R/R_0 has increased to ~1·05 and there is a change of slope of the relationships near this point, after which R/R_0 continues to increase rather less steeply with increasing hydrogen content during the

α- → β-phase hydride transformation until H/Pd reaches ~0·6 and R/R_0 has increased to ~1·68. Fischer found that R/R_0 then remained constant as H/Pd continued to increase up to ~0·8. Slightly different

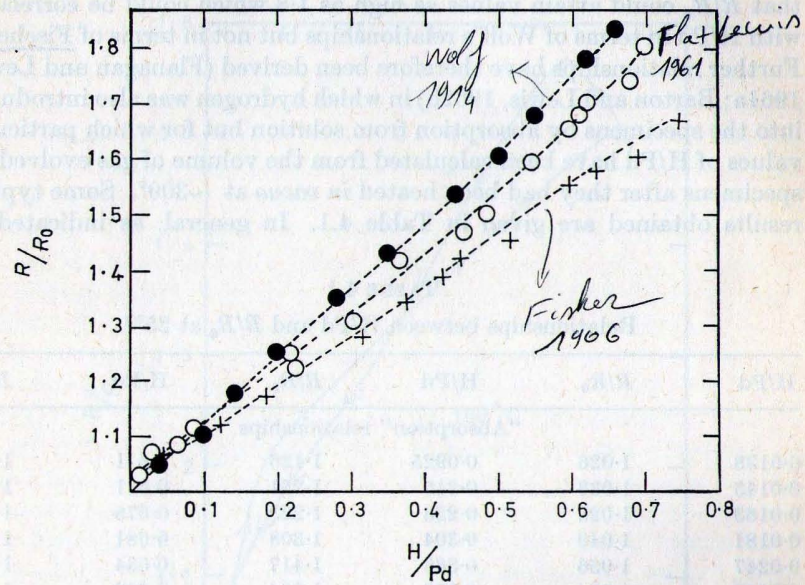


Fig. 4.1 Broad comparison of relationships between H/Pd and R/R_0 using representative results obtained by different authors: +, Fischer (1906) at 18°; ●, Wolf (1914) at 20°; ○, Flanagan and Lewis (1961a) at 25°.

relationships were reported a little later (at 20°) by Wolf (1914) who also took account of concurrent changes of the dimensions of his specimens so that he was able to calculate corresponding changes of specific conductivity. In Wolf's experiments, hydrogen had been absorbed into the specimen directly from the gas phase after its surface had been activated by a series of cycles of electrolytic anodization and cathodization in an apparently analogous procedure to that employed later by Krause and Kahlenberg (1935) and other authors. Again, as indicated in Fig. 4.1, Wolf's relationships between R/R_0 and H/Pd were broadly similar to Fischer's but showed little evidence of a change of slope at H/Pd ~0·025. Wolf also found that R/R_0 could attain values of ~1·8 at H/Pd ~0·7 which was significantly higher than the maximum value recorded by Fischer. Nevertheless, further investigations by other authors in the 1930s (Krüger and Gehm, 1933; Sieverts and Danz, 1937) using a similar electrolytic technique to that of Fischer, appeared to provide a general confirmation of his measurements and

until recently, Fischer's relationships have been those most commonly employed for deriving changes of hydrogen content from measurements of electrical resistance. More recently, however, it has been often found that R/R_0 could attain values as high as 1·8 which could be correlated with H/Pd in terms of Wolf's relationships but not in terms of Fischer's. Further relationships have therefore been derived (Flanagan and Lewis, 1961a; Barton and Lewis, 1962b) in which hydrogen was also introduced into the specimens by absorption from solution but for which particular values of H/Pd have been calculated from the volume of gas evolved by specimens after they had been heated *in vacuo* at ~300°. Some typical results obtained are given in Table 4.1. In general, as indicated in

TABLE 4.1

Relationships between H/Pd and R/R_0 at 25°[1]

H/Pd	R/R_0	H/Pd	R/R_0	H/Pd	R/R_0
"Absorption" relationships					
0·0138	1·026	0·0925	1·126	0·611	1·679
0·0145	1·033	0·215	1·251	0·621	1·695
0·0163	1·028	0·223	1·223	0·678	1·757
0·0181	1·040	0·304	1·308	0·681	1·738
0·0247	1·056	0·366	1·417	0·684	1·747
0·0257	1·054	0·373	1·394	0·692	1·742
0·0272	1·067	0·456	1·467	0·696	1·804
0·0605	1·083	0·485	1·499	0·705	1·799
0·0691	1·074	0·545	1·593	0·709	1·759
0·0851	1·106	0·596	1·654	0·709	1·756
"Desorption" relationships					
0·138	1·16	0·462	1·51	0·543	1·651
0·233	1·23	0·510	1·61	0·561	1·705
0·308	1·35	0·523	1·608	0·593	1·698
0·364	1·40	0·537	1·680	0·648	1·730
0·421	1·46	0·542	1·667	0·684	1·790

[1] After Flanagan and Lewis (1961a), Barton *et al.* (1963a).

Figs 4.1 and 4.2, these recently determined relationships are in quite good agreement with Fischer's for values of H/Pd up to ~0·5, and exhibit an analogous change of slope at values of H/Pd close to α_{max} (0·015–0·025). At higher values of H/Pd, however, there is a divergence from Fischer's relationships and R/R_0 increases to values ~1·8 at values of H/Pd ~0·7, and after passing through a rather flat-topped maximum, R/R_0 decreases again for values of H/Pd > 0·8 (Barton and

Lewis, 1962b). A fully satisfactory explanation is still not available for the lower maximum values which Fischer recorded. It is possible that these discrepancies may be related to the significant changes of the

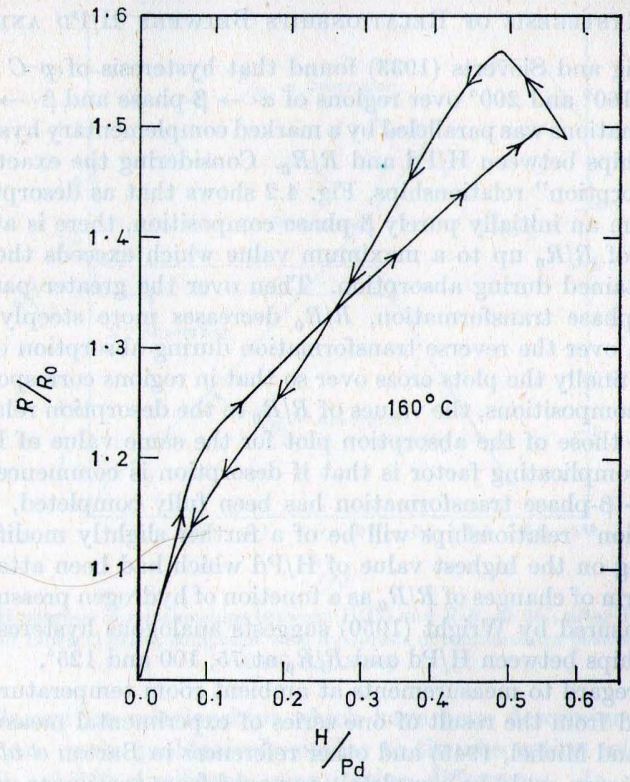


FIG. 4.2 Hysteresis of relationships between H/Pd and R/R_0 at 160°—after Brüning and Sieverts (1933).

electrical resistance of palladium, which can result from annealing under certain conditions and which may be the result of the development of intercrystalline cracks or from the absorption of oxygen (Conybeare, 1937; Raub, 1959).

The present position is that the relationships which have been obtained more recently have been found to correlate satisfactorily with the results obtained in kinetic studies with palladium wires which have been obtained from different sources of supply, provided that their values of specific resistance are in satisfactory accord with the presently accepted values of ~$10·7 \times 10^{-6}$ ohm cm^{-1} at 25° (Flanagan and Lewis, 1961a; Barton *et al.*, 1963a).

Analogous relationships between R/R_0 and D/Pd are discussed in Chapter 8.

B. Hysteresis of Relationships Between H/Pd and R/R_0

Brüning and Sieverts (1933) found that hysteresis of p–C relationships at 160° and 200° over regions of α- → β-phase and β- → α-phase transformations was paralleled by a marked complementary hysteresis of relationships between H/Pd and R/R_0. Considering the exact form of the "desorption" relationships, Fig. 4.2 shows that as desorption proceeds from an initially purely β-phase composition, there is at first an increase of R/R_0 up to a maximum value which exceeds the highest value attained during absorption. Then over the greater part of the β- → α-phase transformation, R/R_0 decreases more steeply than it increased over the reverse transformation during absorption of hydrogen, and finally the plots cross over so that in regions corresponding to α-phase compositions, the values of R/R_0 in the desorption relationship lie below those of the absorption plot for the same value of H/Pd. A further complicating factor is that if desorption is commenced before the α- → β-phase transformation has been fully completed, then the "desorption" relationships will be of a further slightly modified form depending on the highest value of H/Pd which had been attained.

The form of changes of R/R_0 as a function of hydrogen pressure which were measured by Wright (1950) suggests analogous hysteresis of the relationships between H/Pd and R/R_0 at 75, 100 and 125°.

With regard to measurements at ambient room temperature, it was concluded from the result of one series of experimental measurements (Michel and Michel, 1945) and other references in Barton *et al.* (1963a) that hydrogen could be completely removed from specimens which had absorbed hydrogen up to H/Pd ~0·6 without R/R_0 or the other parameters of X-ray lattice constants or magnetic susceptibility showing any concurrent return to values characteristic of pure palladium. Fairly recently, however, these findings seem to have been satisfactorily refuted (Barton *et al.*, 1963a) and in particular a fair number of experimental measurements have been made with which to derive the form of desorption relationships between H/Pd and R/R_0 at 0, 25 and 50° (see Fig. 4.3). In these studies the desorption relationships were also determined after the hydrogen content had been raised during absorption up to a concentration (in equilibrium with a pressure of 1 atm of hydrogen gas) at which the solid had been fully transformed to a β-phase hydride and H/Pd had reached a value exceeding the composition at the point of closure of the corresponding p–C hysteresis loop.

In these studies (Barton *et al.*, 1963a) values of H/Pd were mainly estimated by titrimetric analysis of the extent of reduction of standardized solutions of acidified potassium dichromate.

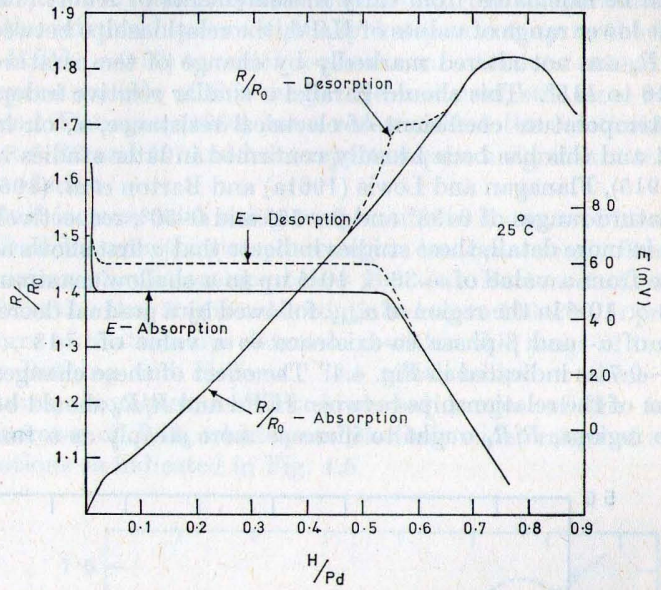


Fig. 4.3 Hysteresis of relationships between H/Pd and R/R_0 at 25°, after Table 4.1 and Barton and Lewis (1962b), compared with hysteresis of relationships between H/Pd and E (cf. Fig. 2.14).

The desorption relationships which have been determined at 0, 25 and 50° are again qualitatively similar to the absorption relationships but still exhibit significant quantitative differences. In particular, Fig. 4.3 shows that there is a "bulge" or "shoulder", where R/R_0 is higher than during absorption—which extends over a range of H/Pd from ~0·35 to ~0·65. As yet, the precision of measurements has not yet been sufficiently high to establish definitely whether, as at from 160 to 200°, there is a "cross-over" of the relationships at low hydrogen contents approaching or corresponding with α-phase regions. There are, however, indications from the form of changes of R/R_0 with time during desorption of hydrogen in solutions of oxidants which do suggest that again this is a likely possibility. (J. C. Barton, unpublished observations.)

C. Temperature Dependence of Relationships Between H/Pd and R/R_0

It can be calculated from early measurements of Knott (1886) that over the lower range of values of H/Pd, the relationships between H/Pd and R/R_0 are not altered markedly by change of temperature over a range 18 to 118°. This should parallel a similar relative independence of the temperature coefficient of electrical resistance, α, on hydrogen content and this has been broadly confirmed in later studies by Beckman (1915), Flanagan and Lewis (1961a) and Barton *et al.* (1963a) over temperature ranges of 0–98° and 0—55° and 0–50°, respectively. Considered in more detail, these studies indicate that α first shows a gradual increase from a value of $\sim 38 \times 10^{-4}$ up to a shallow maximum value of $\sim 42 \times 10^{-4}$ in the region of α_{max}, followed by a gradual decrease over regions of α- and β-phase co-existence to a value of $\sim 18 \times 10^{-4}$ at H/Pd $\sim$0·7 as indicated in Fig. 4.4. The effect of these changes of α on the form of the relationships between H/Pd and R/R_0 should be that in α-phase regions, R/R_0 ought to increase more steeply as a function of

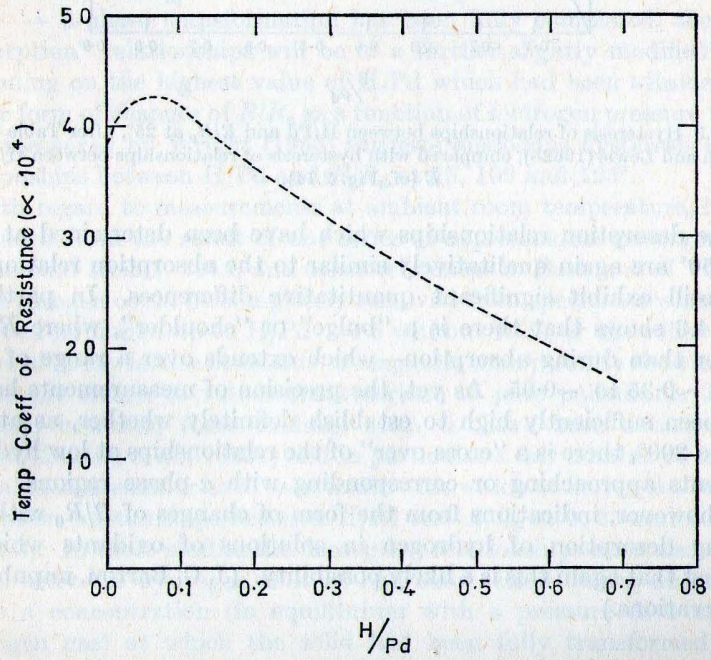


Fig. 4.4 Form of the changes of the temperature coefficient of electrical resistance as a function of hydrogen content at *ca* 25°—after Barton *et al.* (1963a).

hydrogen content as the temperature is raised, and correspondingly less steeply over regions of α- and β-phase co-existence. However, with regard to the α-phase regions, a recent study and analysis by Lindsay and Pement (1962) has indicated that within the temperature range 75–404° the relationships are virtually independent up to the highest value of H/Pd ($\sim$0·10) to which α-phase concentrations extend at the high temperature side of this range. Nevertheless, still more recently Simons and Flanagan (1966) have redetermined the relationships in α-phase at 0, 50 and 90° and have reported quite a significant temperature dependence.

A gradual increase with rising temperature in the rate of increase of R/R_0 with H/Pd over the two-phase region has been clearly illustrated by comparison of relationships below 100° (see Barton *et al.*, 1963a), and confirmation that this trend is continued up to 160–200° is provided by the form of relationships determined within this range of temperatures by Brüning and Sieverts. The relationships at these higher temperatures, moreover, exhibit increased ranges of the initially steeper increase of R/R_0 which parallels their wider range of α-phase concentrations as indicated in Fig. 4.5.

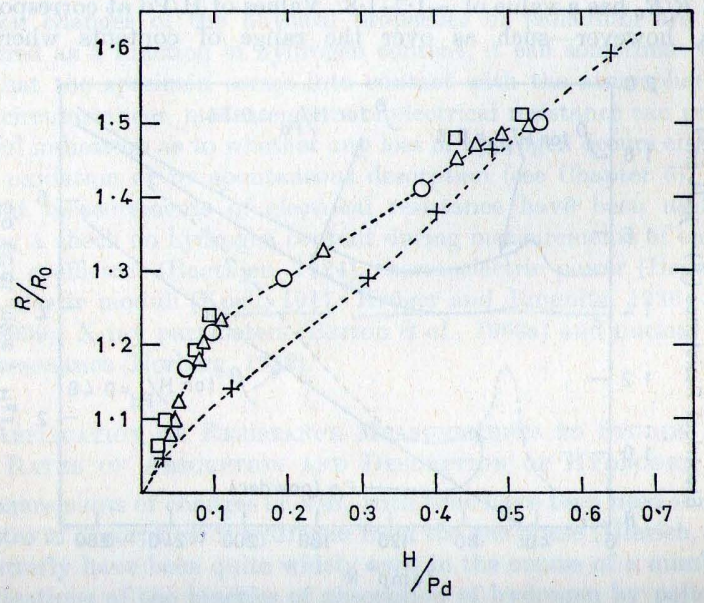


Fig. 4.5 Some further comparisons of "absorption" relationships between H/Pd and R/R_0 at different temperatures: +, Flanagan and Lewis (1961) at 55°; ○, △, □, Brüning and Sieverts (1933) at 160, 180 and 200°, respectively.

Brüning and Sieverts' results also indicate that a further effect of increasing temperature is for the broad maximum in the relationships to occur over steadily lower values of both R/R_0 and H/Pd—compare Figs 4.2 and 4.3. A continuation of this latter trend up to ~470° is suggested by results of Hagen and Sieverts (1933) (who, however, recorded only measurements of equilibrium pressure and not changes of hydrogen content) and by more recent measurements of Levine and Weale (1960) at 366, 396 and 428°. These latter studies indicate that at ~400°, the maximum now occurs at a value of R/R_0 of ~1·5 and at a corresponding value of H/Pd of ~0·4. It might be noted, however, that over lower ranges of H/Pd, Levine and Weale's relationships at 366 and 396° seem somewhat at variance with a continuation of the trends suggested by Brüning and Sieverts' results.

D. Relationships Between H/Pd and R/R_0 at Very Low Temperatures

Relationships have been obtained at as low as 77° K with evaporated palladium films by Suhrmann *et al.* (1959, 1964). These have a similar form to the relationships at 25° in that they pass through a maximum at which R/R_0 has a value of ~1·7–1·8. Values of H/Pd at corresponding stages, however—such as over the range of contents where the

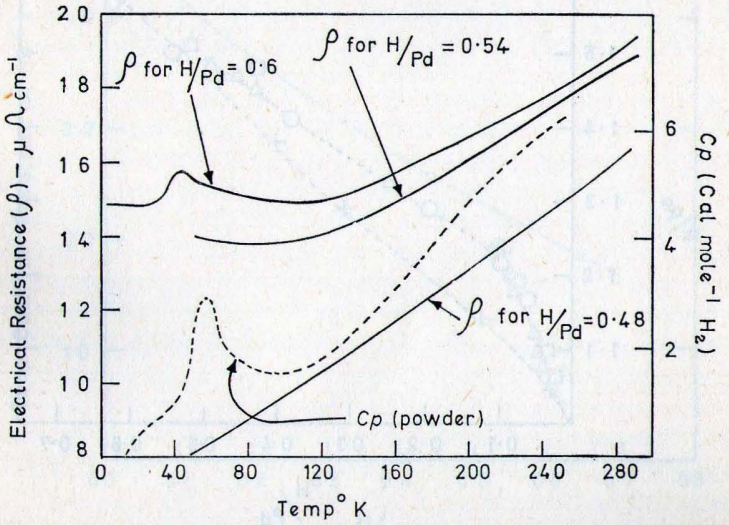


Fig. 4.6 Examples of changes of electrical resistance, ρ, at low temperatures for specimens with differing hydrogen contents, with changes of specific heat (cf. Fig. 2.17) plotted for comparison—after Mitacek and Aston (1963).

maximum in the relationships occur—have been reported to be generally twice as high as *ca* 25°. As has also been discussed in Chapter 2, differences found between the solubilities in films and powders at −77° (196° K) suggest the possibility that the apparent solubilities in the films might be substantially too high.

Measurements at even lower temperatures have been obtained by Schindler *et al.* (1959) with palladium wires which had been changed with hydrogen at higher temperatures. As illustrated in Fig. 4.6, results have shown that at temperatures <55° K there is a very great spread of the values of resistance within a range of hydrogen contents corresponding with H/Pd >0·48 and <0·54. At these low temperatures, specimens with the higher range of contents exhibit much the higher resistances; and for wires in which H/Pd ~0·6, there is clear evidence that the resistance actually passes through a rather shallow maximum over a range of temperatures only a little lower than the range over which λ-type anomalies are obtained in specific heat curves.

E. The Use of Resistance Measurements as an Analytical Guide to Hydrogen Content During Measurements of Other Parameters

When changes of the physical properties of palladium are being measured as a function of hydrogen content, it can sometimes be the case that the specimen comes into contact with the atmosphere. In these circumstances, measurements of electrical resistance can provide a useful indication as to whether any loss of hydrogen occurs either by aerial oxidation or by spontaneous desorption (see Chapter 5). Such conjoint measurements of electrical resistance have been useful in keeping a check on hydrogen content during measurements of changes of Hall coefficient (Raethjen, 1924), thermoelectric power (Heimberg, 1923), elastic moduli (Koch, 1917; Krüger and Jungnitz, 1936; Jungnitz, 1939), X-ray parameters (Barton *et al.*, 1963a) and nuclear magnetic resonance (Norberg, 1952).

F. Application of Resistance Measurements to Studies of Rates of Absorption and Desorption of Hydrogen

Measurements of changes of R/R_0 with time have been used to study the rates of absorption of hydrogen from the gas phase (Ulbrich, 1939) and latterly have been quite widely used in the course of a number of investigations of the kinetics of absorption of hydrogen by palladium electrodes, both during general studies of the absorption of hydrogen molecules dissolved in aqueous solution [see refs. contained in Lewis

(1962b) and Barton and Lewis (1963)] and also recently to study the concurrent rate of absorption of hydrogen during the catalytic decomposition of solutions of formic acid (Burke *et al.*, 1966). Such measurements have been useful in determining the rate-limiting step in the processes of absorption and have also been utilized to determine the coefficient of diffusion of hydrogen within the solid electrodes over the α-phase range of compositions (Simons and Flanagan, 1965a)—see Chapter 7. In the course of these studies in solution, the measurements of resistance have quite frequently been made in conjunction with measurements of electrode potential. It is often convenient to record changes of both parameters with the same potentiometer of voltmeter—and Fig. 4.3 shows that whilst in β-phase regions of composition (H/Pd $>0{\cdot}57$ at *ca* 25°), E is more sensitive than R/R_0 to small changes of H/Pd, R/R_0 is quite a sensitive function of hydrogen content when E is virtually invariant over regions of α- and β-phase co-existence.

By making resistance measurements in electrolytes of low conductance with an alternating current bridge network which is suitably earthed, it has been found possible to follow the courses of the absorption of hydrogen by palladium electrodes actually during electrolysis. This technique has been employed in studies of the electrolytic reduction of ethylene and acetylene, and in studies of the limiting amounts of hydrogen which can be absorbed during electrolysis by cathodes of palladium and palladium alloys of differing surface activities (Barton and Lewis, 1962b; Green and Lewis, 1964).

Measurements of changes of R/R_0 have also been employed to study the kinetics of desorption and oxidation of hydrogen from specimens whose initial contents generally corresponded to β-phase compositions. Studies have been made of both the behaviour of a number of inorganic oxidants (Knorr 1931; Breiter *et al.*, 1956; Barton *et al.*, 1963b) and also of the effects of ethylene and acetylene (Burke *et al.*, 1964). The results are discussed in the next chapter.

G. Errors in Measurements of the Electrical Resistance of Specimens Immersed in Solution due to Co-conduction of the Measuring Current Through the Electrolyte

Specimens immersed in electrolytic solution can provide a parallel path for conduction of the bridge current. Clearly, the relative proportion of current passing through the electrolyte will be higher in strong electrolytes and for specimens of high electrical resistance. The total impedance through the electrolyte is made up of the impedance of the bulk of the solution together with the impedance at the interface

between the specimen and the solution. This interface impedance is generally lower at surfaces which are catalytically active for dissociation of hydrogen molecules so that, other things being equal, errors in resistance measurements which arise from "co-conduction" effects can be especially significant under these conditions. When the resistance of such surface-active specimens is being measured by a direct current method while immersed in strongly acid solutions, its apparent value has been found to markedly "drift up", i.e. to increase with time (Knorr and Schwartz, 1933, 1934). This has been shown to reflect the fact that the effect of the voltage drop across the specimen, associated with the passage of current through it, is to cause hydrogen to be transferred from one end of the specimen to the other, and that the resultant differences of hydrogen content give rise to a gradually increasing e.m.f. which, at the limit, is such as virtually to polarize further transfer of hydrogen and cause the apparent value of electrical resistance to approach quite close to its true value (Carson *et al.*, 1960). Such polarization will build up more rapidly when the initial hydrogen content of the specimen falls within a range where small changes of H/Pd are complementary with continuous changes of electrode potential such as in purely α- or β-phase regions. Even in these regions, however, absolutely complete polarization is prevented by the fact that there can be a continuous overall drain of hydrogen from the high hydrogen-content side of the specimen due to a higher overall rate of desorption of hydrogen molecules from this side into the solution. This loss of hydrogen by desorption has to be continually replaced by a continued electrolytic hydrogen transfer between the ends of the specimen corresponding to what can be termed a steady-state residual current, so that, complementarily, the apparent resistance can still be less than true by a small amount.

Furthermore, when the overall hydrogen content of the specimen corresponds to regions where α- and β-phase hydrides co-exist, it is even more difficult to polarize co-conduction of the bridge current by hydrogen transfer. This is because in these regions the electrode potential is virtually invariant with changes of hydrogen content so that very substantial quantities of hydrogen would have to be transferred before virtual polarization was complete. As a consequence, the apparent value of resistance could remain at a value substantially lower than true for complementarily long periods—and, furthermore, the alloy could finally be markedly inhomogeneous in terms of hydrogen content. Results have been published (Carson *et al.*, 1960) of the sequence of changes of both the sign and magnitude of errors in concurrent measurements of resistance made during the absorption

of hydrogen by palladium wires until they had been fully transformed to β-phase compositions.

It may be noted in passing, however, that investigation into the source of these errors in resistance measurements has led to the initiation of studies of the electrolytic transfer of hydrogen between electrodes of palladium and palladium alloys in their own right—both to find out more information about the kinetics of the transfer process, and also because pairs of such electrodes can in principle form the plates of a somewhat unique type of electrical storage cell (Barton *et al.*, 1963c; Lewis, 1963).

As a further extension of the problem of co-conduction, it has been found (Barton *et al.*, 1963b) that the apparent value of the resistance can exhibit continuous erratic variations during measurements of the rate of removal of hydrogen from previously hydrided palladium wires by well-stirred and quite acidic solutions of oxidants. This appears to be the result of local variations of hydrogen content giving rise in turn to transitory local cell potentials along the length of the wire. Even in these cases, however, a useful guide to the course of the reaction was provided by measurements of resistance made at intervals during an experiment while the specimen was temporarily transferred to a container of distilled water. A similar procedure has also been used to provide a general check on other occasions where it has been suspected that the apparent value of the resistance could be in error because of co-conduction effects. In deriving relationships between hydrogen content and electrical resistance for some palladium alloys (Barton *et al.*, 1966a), complete experimental runs have been repeated in distilled water as well as in dilute acid solutions to ensure that certain details of the relationships could not have been merely an apparent result of hydrogen-transfer phenomena.

In measurements with A.C. bridge networks, the capacitive component of the impedance through the electrolyte can act as an effective short-circuit to an increasing extent with increase of the A.C. frequency. The net results, without any careful simulation of the equivalent components of the interface impedance in the balance arm, is that the apparent value of resistance again is generally too low and is most markedly the case for high frequencies. As a result, there can be a marked spread of apparent resistance with frequency in strongly conducting solutions (Barton and Lewis, 1962a). Nevertheless, the effects of co-conduction can be relatively negligible in more dilute acid solutions and quite accurate measurements of resistance with A.C. bridge networks have been obtained (Barton and Lewis, 1962b; Green and Lewis, 1966a, b).

CHAPTER 5

Chemical Stability of Hydrided Palladium

A. The Use of Measurements of Physical and Physico-chemical Parameters for Estimations of Gain and Loss of Hydrogen

In many experiments involving hydrided palladium it is a considerable advantage to have a reliable knowledge of the hydrogen content of specimens at all times.

During direct experimental derivation of p-C-T relationships, changes of hydrogen content can, of course, be calculated from the volumes of gas admitted and from changes of pressure. In a broadly analogous technique, the hydrogen contents of specimens which have relatively inactive surfaces at lower temperatures can also be estimated from the volumes of gas evolved after they have been heated *in vacuo* at $\sim 300°$ (Bennett, 1939; Barton *et al.*, 1966a). Again, in experiments where hydrogen is introduced into the specimens electrolytically, the volumes of hydrogen absorbed by palladium cathodes can be estimated from the total amount of current passed and the volume of hydrogen evolved simultaneously as gas which can be collected in forms of gas burettes—provided proper allowance is made for several sources of error.

There can, however, be numerous experimental circumstances when changes of hydrogen content can only be calculated by less direct methods such as by the measurement of some physico-chemical or physical parameter of the surface and/or of the bulk, for which a relationship with hydrogen content has previously been well established.

A number of such parameters have been employed as guides to changes of hydrogen content during the absorption of hydrogen. In studies where the palladium is immersed in solution, electrode potential measurements have latterly been widely utilized, and the physical parameters which have been used have even included changes of weight (Dewar, 1873) and, more recently, magnetic susceptibility (Norberg, 1952), mechanical hardness (Sugeno and Kowaka, 1954; Tiedema *et al.*, 1959) and measurements of X-ray parameters (Tiedema

et al., 1960; Aben and Burgers, 1962). Whether the specimen has been immersed in solution or not, it has, however, been changes of electrical resistance which have most often been employed—various examples have been cited and discussed in the previous chapter.

The utility of these same physical parameters as a guide to changes of hydrogen content during the *removal* of hydrogen was for some time rather suspect in view of the findings by one group of investigators (see Chaudron *et al.*, 1938; Bénard and Talbot, 1939 and compare Cupp, 1953) that X-ray parameters, magnetic susceptibility and electrical resistance could remain at values characteristic of β-phase hydrides even after complete removal of hydrogen at room temperature.

Latterly, however, it has been shown that these findings were erroneous (Barton *et al.*, 1963a; also Vert *et al.*, 1965; Sugeno and Kowaka, 1954); and that similar relationships between hydrogen content and many other of the various parameters are likely to apply during both absorption and desorption with relatively minor differences [see, however, Sugeno and Kowaka's findings (1954) for changes of hardness as discussed in Chapter 3 and illustrated in Fig. 3.2] corresponding with hysteresis associated with α- → β-phase and β- → α-phase transformations.

B. Chemical Stability of Specimens with Highly-active Surfaces in Contact with the Gaseous Phase

As is discussed in Chapters 3 and 7, the diffusion of hydrogen is sufficiently rapid, even at and below room temperature, to make it quite a convenient practical possibility for p–C–T relationships to be obtained—provided, however, that the surfaces of the specimen have a sufficiently high catalytic activity for dissociation of hydrogen molecules. In the case of fairly massive forms of palladium, quite a high catalytic activity in this regard has been obtained following upon activations by glow discharge in argon (Ulbrich, 1939; Jewett and Makrides, 1965) or by cycles of alternate electrolytic charging and rapid desorption by heating to redness (Krause and Kahlenberg, 1935). In general, however, the ability of such specimens to equilibrate readily with gaseous hydrogen often tends to show a rapid decline on standing, and it therefore seems likely that hydrogen absorbed into even these specimens could become more or less irreversibly absorbed in a practical sense after the hydrided specimen had been aged for some time. At present, measurements related to spontaneous decomposition and the corresponding development of a "desorption" hydrogen pressure have been reported at temperatures $< ca$ 100° only for specimens which were in the form of finely divided palladium blacks (Nace and Aston, 1957; Wicke and Nernst, 1964) or in the form of evaporated metal films (Suhrmann *et al.*, 1964). Such surfaces would, *ad hoc*, be expected also to be active catalytically for reactions between the absorbed hydrogen and other species (e.g., unsaturated hydrocarbons) which may react quite rapidly with gaseous hydrogen in the presence of an equivalently active palladium catalyst (Cremer *et al.*, 1941; Dubuichin and Frost, 1946). One related experimental observation is that the hydrogen contained in palladium wire electrodes which had been coated with palladium black could be so rapidly oxidized after the specimen had been dried out in the atmosphere that they were momentarily raised to red heat (J. A. S. Green, unpublished). The atmospheric oxidation of the hydrogen in palladium had been noted, however, in his initial studies by Graham (1868) and also in other early work (see, e.g., Troost and Hautefeuille, 1874).

C. Stability of Specimens with Highly-active Surfaces Immersed in Aqueous Solutions

Somewhat more detailed information is available concerning the reactivity of electrodes immersed in aqueous solutions at around room temperature.

In this case determinations of the rates of both absorption and desorption of hydrogen (Barton *et al.*, 1963b) from measurements of electrode potential and electrical resistance have shown that surfaces can be obtained of a sufficiently high catalytic activity for both the gain and loss of hydrogen to be governed by transport of hydrogen molecules through interfacial layers of solution. Such highly-active surfaces can be obtained by electroplating on a thin layer of palladium black and also have been obtained subsequent to the reduction of thin layers of oxide which had been formed either by heating in oxygen or by electrolytic anodization. Hydrided electrodes with such a high surface activity can spontaneously lose hydrogen into a hydrogen-free solution at a rate which is dependent on the conditions of stirring and is proportional to the equivalent hydride vapour pressures as derived from the measurements of electrode potential.

Rates of removal of hydrogen from specimens in the form of wires with palladized surfaces (coated with palladium black) by chemical oxidation have been obtained with a number of oxidants from measurements of changes of electrode potential and relative electrical resistance (Barton *et al.*, 1963b; Burke *et al.*, 1964). With oxygen and hydrogen peroxide (Barton *et al.*, 1963b) and with ethylene (Burke *et al.*, 1964),

it has been found that oxidative removal of hydrogen can proceed sufficiently rapidly at all values of hydrogen content, for the rate again to be controlled primarily by transport of the oxidant through solution to the surface of the specimens as in the example of results illustrated in Fig. 5.1 (also Anderson and Eyring, 1963) or else, in the case of high

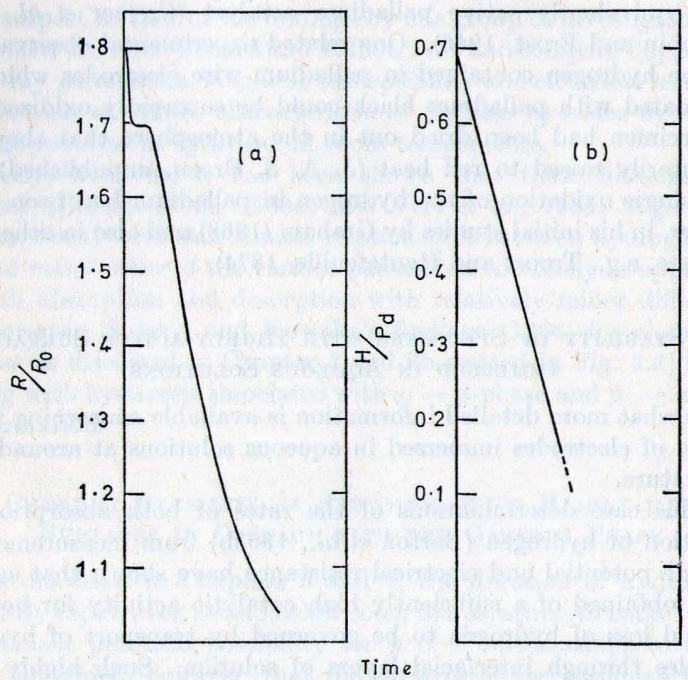


FIG. 5.1 Comparison of changes of R/R_0 [in (a)] and corresponding changes of H/Pd [in (b)] with the same arbitrary time scale, for removal of hydrogen from previously hydrided palladium at 25° under conditions where the kinetics are governed by transport of oxidant to the surface—after Barton *et al.* (1963b), Burke *et al.* (1964).

concentrations of oxidant, by the diffusion of the hydrogen in the solid substrate to the surface. This has also been found to be the case for oxidation by solutions of potassium permanganate, potassium dichromate or ceric sulphate, provided that solutions were sufficiently acidic in order to either prevent hydrolysis in the case of ceric sulphate or to dissolve surface oxides of chromium or manganese which can form as intermediate products. [Solutions of potassium dichromate and ceric sulphate have both been used for estimating hydrogen contents by titrimetric analysis (Barton *et al.*, 1963b)].

Similar conclusions broadly apply to results obtained with chlorine–

saturated solutions except that this reagent can also severely attack the palladium itself. In the case of solutions of bromine, however, there is only partial removal of hydrogen before an inhibitory effect occurs, and an iodine solution acts as a virtually immediate inhibitor. With reference to this behaviour of iodine, prior immersion of hydrogen-free specimens in solutions of iodine also had an inhibitory effect on the subsequent absorption of hydrogen—but, after being heated in an oxy-coal gas flame, surfaces which were highly active for absorption of hydrogen were re-obtained (Barton *et al.*, 1966b), so that iodine seems a less irreversible inhibitor than poisons such as sulphur or arsenic (see Shashkina and Kulakova, 1963; Green and Lewis, 1964).

Measurements of the rates of removal of hydrogen by acetylene dissolved in aqueous solutions (Burke *et al.*, 1964) suggested that this reaction can lead to the formation of polymeric hydrocarbon species which are partly but not completely inhibitory. In this latter connection, it may be noted that the gradual formation of inhibiting carbonaceous polymeric films also seems to provide the most probable explanation of the gradual inhibition of the decomposition of formic acid at palladium electrodes (Burke *et al.*, 1966). Although the reaction of this compound is in a sense opposite to that of acetylene in that as shown in Fig. 5.2, initially there can be an appreciable overall absorption of hydrogen. Measurements of changes of electrical resistance have shown, however, that, if the solution is continuously swept out by a bubbled stream of argon, this initial absorption is followed finally by a

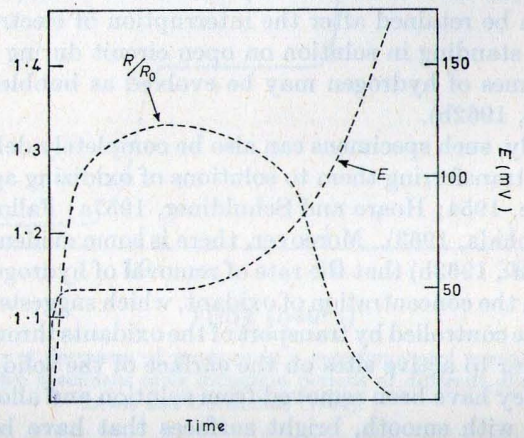


FIG. 5.2 An example of the form of changes of R/R_0 and electrode potential after immersion of an initially hydrogen-free palladized palladium wire in argon-saturated formic acid at 25° indicating an initial absorption followed by spontaneous desorption—after Burke *et al.* (1966).

spontaneous desorption of all of this hydrogen. This follows from the fact that the poisoning is fairly selective and the specimen can retain a relatively high level of activity for equilibration with molecular hydrogen.

D. Stability of Specimens with Surfaces Which are Relatively Inactive for Equilibration with Hydrogen Molecules

As also discussed in Chapters 1, 2 and 7, specimens with "smooth" "bright" surfaces generally have relatively poor catalytic activities for equilibration with hydrogen gas at around room temperature when in the "as received" condition after manufacture. Again, except after oxidative activation, electrodes of such a smooth, bright form generally also have a low activity for equilibration with hydrogen molecules dissolved in solution.

Nevertheless, hydrogen can still be introduced into such electrodes by electrolysis. Although fully systematic studies are not available, the course of absorption is generally irreproducible, and considerable volumes of hydrogen can be evolved simultaneously even at low current densities and low hydrogen contents. The quantity of hydrogen which is finally absorbed in the steady-state may in fact substantially exceed the quantity of hydrogen which can be absorbed by electrodes with surfaces of a high activity for equilibration with hydrogen molecules (Barton and Lewis, 1962b; Green and Lewis, 1964) and much of this can be retained after the interruption of electrolysis even after prolonged standing in solution on open circuit during which relatively large volumes of hydrogen may be evolved as bubbles of gas (Barton and Lewis, 1962b).

Generally, such specimens can also be completely dehydrided by subsequently transferring them to solutions of oxidizing agents (Lewis and Ubbelohde, 1954; Hoare and Schuldiner, 1957a; Fallon and Castellan, 1960; Tsuchida, 1963). Moreover, there is some evidence (Knorr, 1931; Barton *et al.*, 1963b) that the rate of removal of hydrogen again depends directly on the concentration of oxidant, which suggests that the kinetics may still be controlled by transport of the oxidants through the Brünner–Nernst layer to active sites on the surface of the solid.

After they have been removed from solution and allowed to dry, such specimens with smooth, bright surfaces that have been loaded with hydrogen by electrolysis can exhibit more prolonged periods of inhibition of aerial oxidation than palladized specimens. This has proved of some practical advantage when it has been experimentally convenient to

be able to transfer specimens through the atmosphere without an appreciable loss of hydrogen—for example, prior to estimations of hydrogen content by the method of outgassing *in vacuo* when deriving relationships between hydrogen content and physical parameters (Flanagan and Lewis, 1959; Maeland and Flanagan, 1964; Barton *et al.*, 1966a).

However, although occurring more slowly than the rapid atmospheric oxidation of the palladized specimens, Fig. 5.3 illustrates that analogous

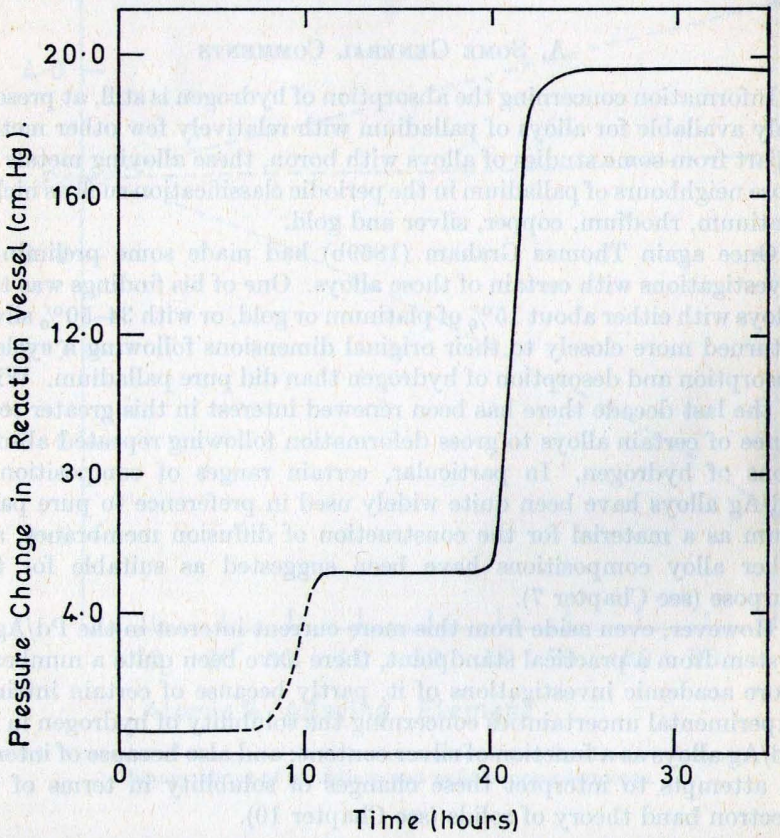


Fig. 5.3 An example of decreases of pressure in a reaction vessel resulting from the aerial oxidation of two specimens after induction periods of different duration—after Lewis and Ubbelohde (1954).

aerial oxidation of the smooth specimens can sometimes occur relatively quickly after induction periods of quite widely varying duration (Lewis and Ubbelohde, 1954).

CHAPTER 6

Absorption of Hydrogen by Alloys of Palladium

A. Some General Comments

Information concerning the absorption of hydrogen is still, at present, only available for alloys of palladium with relatively few other metals. Apart from some studies of alloys with boron, these alloying metals are close neighbours of palladium in the periodic classification such as nickel, platinum, rhodium, copper, silver and gold.

Once again Thomas Graham (1869b) had made some preliminary investigations with certain of these alloys. One of his findings was that alloys with either about 15% of platinum or gold, or with 34–50% silver, returned more closely to their original dimensions following a cycle of absorption and desorption of hydrogen than did pure palladium. Within the last decade there has been renewed interest in this greater resistance of certain alloys to gross deformation following repeated absorptions of hydrogen. In particular, certain ranges of composition of Pd/Ag alloys have been quite widely used in preference to pure palladium as a material for the construction of diffusion membranes, and other alloy compositions have been suggested as suitable for this purpose (see Chapter 7).

However, even aside from this more current interest in the Pd/Ag/H system from a practical standpoint, there have been quite a number of more academic investigations of it, partly because of certain intrinsic experimental uncertainties concerning the solubility of hydrogen in the Pd/Ag alloys as a function of silver content; and also because of interest in attempts to interpret these changes of solubility in terms of the electron band theory of solids (see Chapter 10).

B. Crystal Structures of the Hydrogen-free Alloys

It is a possibility that several of the alloys which have been investigated could theoretically form ordered structures such as Pd_3Au at temperatures less than about 500 or 600° (Raub, 1959). Generally, however, the indications are that such ordering could only take place

after very prolonged annealing at these temperatures. This is suggested by the fact (see Fig. 6.1) that plots of X-ray parameter against composition for binary alloys with other elements of f.c.c. symmetry exhibit only relatively minor deviations from a linear (i.e., Vegard Law) relationship, (see Coles, 1956; Axelrod and Makrides, 1964; Maeland

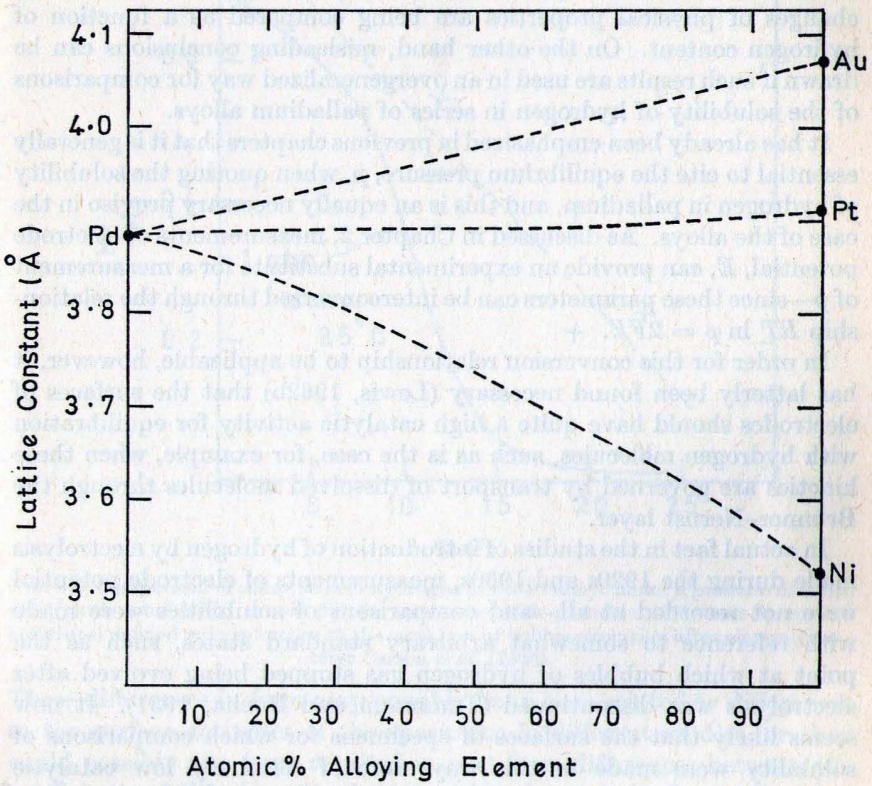


Fig. 6.1 Examples of changes of f.c.c. lattice constant as a function of composition for binary alloys of palladium and neighbouring elements.

and Flanagan, 1964; Bidwell and Speiser, 1964). Thus, leaving aside the problem of palladium/boron alloys, the majority of alloys which have so far been studied with regard to absorption of hydrogen generally have been regarded as substitutional solid solutions in which palladium and the other element are virtually interchangeable on any lattice site over the whole range of compositions.

C. Absorption of Hydrogen During Electrolytic Discharge and Subsequent Comparisons of the Solubility of Hydrogen as a Function of Alloy Composition

In most studies, until about the last ten years, hydrogen had been introduced into palladium alloys by electrolysis.

The use of this technique creates no really basic problems when only changes of physical properties are being compared as a function of hydrogen content. On the other hand, misleading conclusions can be drawn if such results are used in an overgeneralized way for comparisons of the solubility of hydrogen in series of palladium alloys.

It has already been emphasized in previous chapters that it is generally essential to cite the equilibrium pressure, p, when quoting the solubility of hydrogen in palladium, and this is an equally necessary proviso in the case of the alloys. As discussed in Chapter 2, measurements of electrode potential, E, can provide an experimental substitute for a measurement of p—since these parameters can be interconverted through the relationship $RT \ln p = 2FE$.

In order for this conversion relationship to be applicable, however, it has latterly been found necessary (Lewis, 1962b) that the surfaces of electrodes should have quite a high catalytic activity for equilibration with hydrogen molecules, such as is the case, for example, when these kinetics are governed by transport of dissolved molecules through the Brünner–Nernst layer.

In actual fact in the studies of introduction of hydrogen by electrolysis made during the 1920s and 1930s, measurements of electrode potential were not recorded at all—and comparisons of solubilities were made with reference to somewhat arbitrary standard states, such as the point at which bubbles of hydrogen gas stopped being evolved after electrolysis was discontinued (Tammann and Rocha, 1931). It now seems likely that the surfaces of specimens for which comparisons of solubility were made in this way were of relatively low catalytic activity for equilibration with hydrogen. Thus, for instance, the solubilities of hydrogen in Pd/Pt and Pd/Rh alloys reported by Tammann and Rocha (1931) have now been shown (Fig. 6.2), by comparison with more recently derived p–C–T relationships (Carson *et al.*, 1960; Barton *et al.*, 1966a), probably to correspond with equilibrium pressures which are in excess of the upper limits of pressures equivalent to the steady-state concentrations of hydrogen at *catalytically-active* electrodes during electrolysis (Green and Lewis, 1964, 1966a).

Moreover, considering in particular the Pd/Ag/H system, different investigators have reported marked variations in the general form of

relationships between silver content and solubility of hydrogen as defined in similarly arbitrary ways following electrolysis (Smith, 1948).

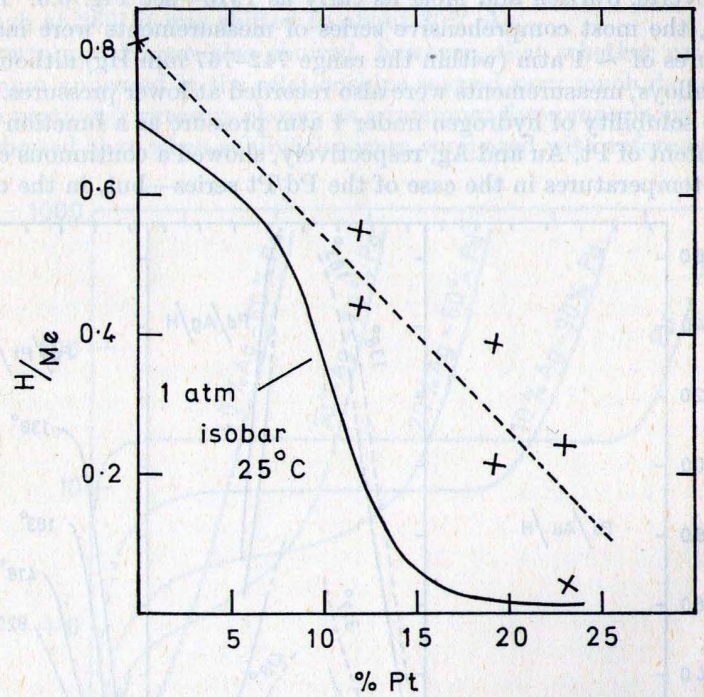


Fig. 6.2 Comparison of solubilities of hydrogen in Pd/Pt alloys under a pressure of 1 atm (25°), with solubilities, ×, (at 20° for specimens with probable differences in surface activities) defined with reference to the cessation of bubble evolution after electrolysis—after Carson *et al.* (1960).

These differences in form may possibly have been related to differences in the surface activities of the specimens in different studies, or they could possibly also have resulted in part from differences between the coefficients of diffusion of hydrogen within the various alloys. However this may be, there now seems little to be gained from unduly prolonged speculation into the causes of these differences in form, which have given rise to what can now be seen as fundamentally barren controversy in view of the lack of definition of any reference of pressure for comparisons of solubility.

D. Direct Derivation of p–C–T Relationships for Alloys

Despite the preponderance of investigations of alloy systems by electrolytic methods in the 1920s and 1930s one study of equilibria set

up directly between hydrogen gas and some Pd/Pt, Pd/Au and Pd/Ag alloys at a series of temperatures from 138 to 826° had been carried out by Sieverts, Jurisch and Metz as early as 1915—see Fig. 6.3. In this study, the most comprehensive series of measurements were made at pressures of ~ 1 atm (within the range 742–767 mm Hg) although for some alloys, measurements were also recorded at lower pressures. Plots of the solubility of hydrogen under 1 atm pressure as a function of the % content of Pt, Au and Ag, respectively, showed a continuous decline at all temperatures in the case of the Pd/Pt series—but, in the case of

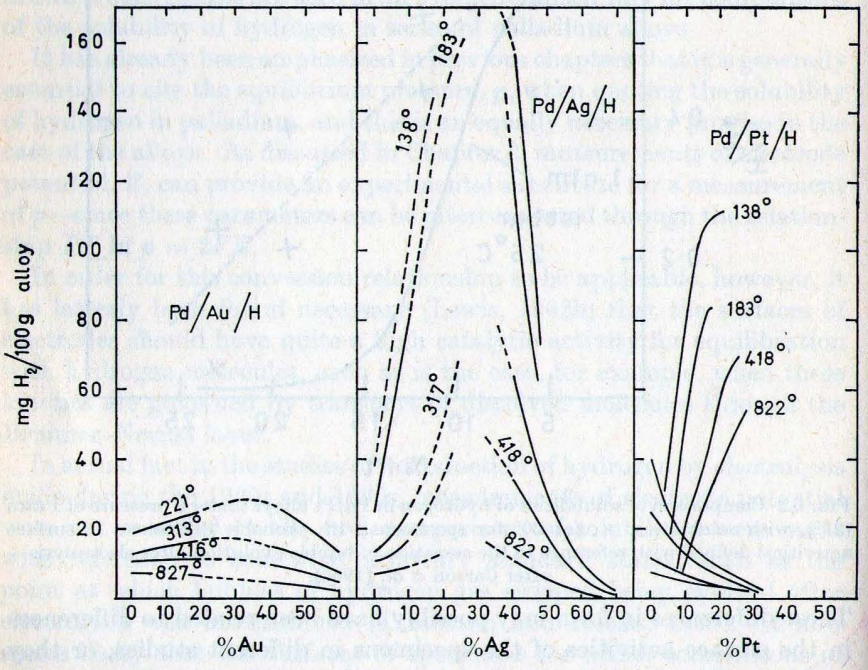


FIG. 6.3 Comparison of solubilities of hydrogen under a pressure of 1 atm in series of palladium alloys—from measurements of Sieverts, Jurisch and Metz (1915).

the Pd/Au alloys and particularly in the case of the Pd/Ag series, exhibited pronounced maxima which became less marked with increasing temperature but were still perceptible at 416° in the case of Pd/Au alloys and at 821° in the case of the Pd/Ag alloys. The maxima seemed to occur within a range of compositions of from 20 to 40% of Ag or Au and, with increasing temperature, seemed to be shifting slightly towards a lower percentage content of the alloying metal.

In the case of the Pd/Ag/H system, these results were broadly confirmed by later studies of Sieverts and Hagen (1935) made at 155, 200

and 260° using pressures of hydrogen of up to ~ 8·2 atm. However, at 155 and 200°, the maximum in the solubilities (again compared with reference to a pressure of 1 atm) was now found to be closer to 20% Ag, although at 260° it was shifted to about 30% Ag.

Sieverts and Hagen also showed, however, that whether or not a maximum appeared in the relationships seemed very much dependent on the particular pressure chosen as a reference for comparisons. Thus they showed that when solubilities were compared with reference to a

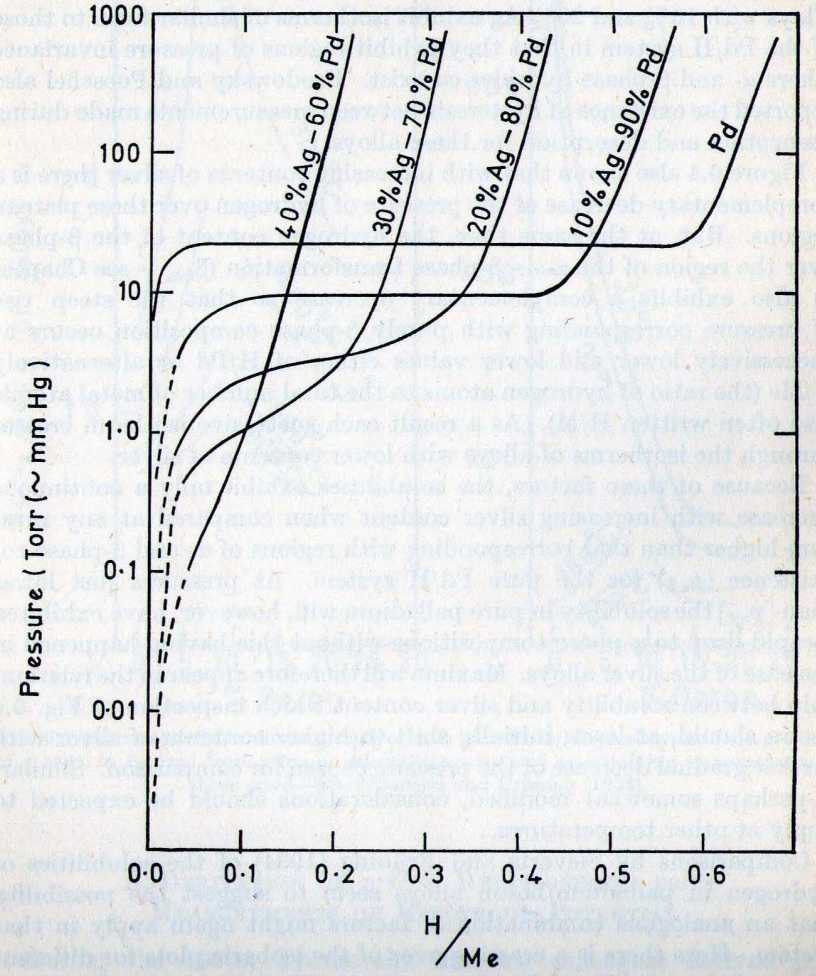


FIG. 6.4 Comparison of p–C (absorption) relationships for palladium/silver alloys at 50°—after Brodowsky and Poeschel (1965).

pressure of ~ 5·5 atm that there was still an apparent maximum at 155° at about 5% Ag, but at 200° there was apparently a continuous decline of solubility with increasing silver content.

It now seems possible to get a better understanding of these earlier findings from more recent studies of Brodowsky and Poeschel (1965) extending over a comprehensive series of pressures within a range from 0·1 mm up to 760 mm Hg at temperatures within the range 30–148°. Figure 6.4 illustrates Brodowsky and Poeschel's isothermal relationships at 50° and shows, as also found by Sieverts and Hagen (1935), that the alloys with 10% and 20% Ag exhibit isotherms of similar form to those of the Pd/H system in that they exhibit regions of pressure invariance where α- and β-phase hydrides co-exist. Brodowsky and Poeschel also reported the existence of hysteresis between measurements made during absorption and desorption for these alloys.

Figure 6.4 also shows that with increasing contents of silver there is a complementary decrease of the pressure of hydrogen over these plateau regions. But, at the same time, the hydrogen content of the β-phase over the region of the α- → β-phase transformation (β_{min} —see Chapter 2) also exhibits a complementary decrease so that the steep rise of pressure corresponding with purely β-phase composition occurs at successively lower and lower values either of H/Pd or alternatively H/Me (the ratio of hydrogen atoms to the total number of metal atoms, also often written H/M). As a result each successive isotherm crosses through the isotherms of alloys with lower contents of silver.

Because of these factors, the solubilities exhibit only a continuous decrease with increasing silver content when compared at any pressure higher than that corresponding with regions of α- and β-phase co-existence ($p_{\alpha,\beta}$) for the pure Pd/H system. At pressures just lower than [$p_{\alpha,\beta}$] the solubility in pure palladium will, however, have exhibited a rapid drop to α-phase compositions without this having happened in the case of the silver alloys. Maxima will therefore appear in the relationship between solubility and silver content which inspection of Fig. 6.4 shows should, at least, initially shift to higher contents of silver with further gradual decrease of the pressure chosen for comparison. Similar, if perhaps somewhat modified, considerations should be expected to apply at other temperatures.

Comparisons by Sieverts and Brüning (1934) of the solubilities of hydrogen in palladium/boron alloys seem to suggest the possibility that an analogous combination of factors might again apply in that system. Here there is a crossing over of the isobaric plots for different alloys of the solubility of hydrogen (in equilibrium with a pressure of 1 atm H_2) as a function of temperature. Correspondingly, there are

maxima in plots of the solubilities against percentage content of boron at about 5–10% boron over a range of temperature from about 160 to 800° as shown in Fig. 6.5.

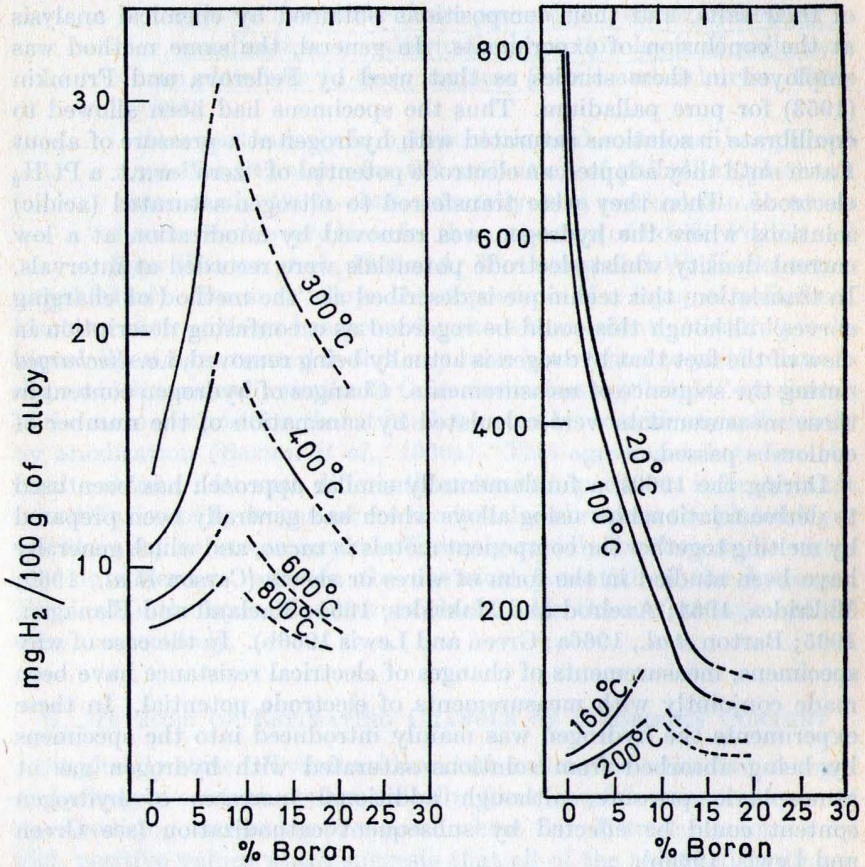


FIG. 6.5 Estimates of solubilities of hydrogen in palladium/boron alloys under a pressure of 1 atm, as derived from plots of solubilities measured at adjoining temperatures to those cited—after Sieverts and Brüning (1934).

E. Derivation of p-C-T Relationships from Measurements of Electrode Potential

During the 1950s, Tverdovskii and his colleagues derived p-C relationships for alloys of palladium with Ag (Vert and Tverdovskii, 1954); Ni (Tverdovskii and Vert, 1953); Rh (Tverdovskii and Stetsenko,

1952); Pt (Stetsenko and Tverdovskii, 1952) and Cu (Karpova and Tverdovskii, 1959) from experimentally determined relationships between electrode potential and hydrogen content. These "alloys" had been prepared by co-precipitation of the metals from mixed solutions of their salts, and their compositions obtained by chemical analysis at the conclusion of experiments. In general, the same method was employed in these studies as that used by Federova and Frumkin (1953) for pure palladium. Thus the specimens had been allowed to equilibrate in solutions saturated with hydrogen at a pressure of about 1 atm until they adopted an electrode potential of "zero" w.r.t. a Pt/H_2 electrode. Then they were transferred to nitrogen-saturated (acidic) solutions where the hydrogen was removed by anodization at a low current density whilst electrode potentials were recorded at intervals. In translation, this technique is described as "the method of charging curves" although this could be regarded as a confusing description in view of the fact that hydrogen is actually being removed, i.e. *discharged* during the sequence of measurements. Changes of hydrogen content in these measurements were calculated by summation of the number of coulombs passed.

During the 1960s, a fundamentally similar approach has been used to derive relationships using alloys which had generally been prepared by melting together the component metals *in vacuo*, and which generally have been studied in the form of wires or sheets (Carson *et al.*, 1960; Makrides, 1964; Axelrod and Makrides, 1964; Maeland and Flanagan, 1965; Barton *et al.*, 1966a; Green and Lewis 1966b). In the case of wire specimens, measurements of changes of electrical resistance have been made conjointly with measurements of electrode potential. In these experiments the hydrogen was mainly introduced into the specimens by being absorbed from solutions saturated with hydrogen gas at atmospheric pressure, although additional increases of hydrogen content could be effected by subsequent cathodization (see Green and Lewis, 1966b).

F. Activation of Electrodes

As with pure palladium (see Chapter 2), unambiguously reproducible measurements of changes of electrode potential with time—or hydrogen content—during absorption of hydrogen seem only to have been obtained with specimens which are highly catalytically-active for equilibration with the dissolved hydrogen. Generally, surfaces seem to have a sufficiently high overall catalytic activity for such reproducibility to occur when the kinetics of gain and loss of hydrogen is governed by

transport of hydrogen molecules through the Brünner–Nernst boundary layer.

The methods of obtaining such active surfaces, in general, have been the same as those used in analogous experiments with pure palladium. That is the specimens have either been preoxidized, either by heating in oxygen or by anodization, or, alternatively, a thin layer of palladium black has been plated on to their surfaces (Lewis and Schurter, 1960; Makrides, 1964).

Anodization, particularly in hydrochloric acid solutions, has proved quite a successful technique for the activation of palladium/platinum alloys (Carson *et al.*, 1960)—but, generally, this method can be much less relied on to work every time for the activation of Pd/Ni, Pd/Rh and Pd/Ag alloys (Barton *et al.*, 1966a; A. W. Carson and W. H. Schurter, unpublished). For such alloys the deposition of a layer of palladium black on their surfaces has proved quite a convenient activating technique. Specimens treated in this way have been found to yield relationships which are closely similar to those derived using "bright" specimens of the same composition that it has been possible to activate sufficiently by anodization (Barton *et al.*, 1966a). This agreement between the results obtained for such differently activated specimens indicates that interdiffusion of hydrogen across the interface between the plated layer and the alloy substrate occurs sufficiently rapidly for there to be virtually no difference between the chemical potential of the hydrogen dissolved in the layer of palladium black and in the surface layers of the alloy, respectively.

G. Methods of Estimating Changes of Hydrogen Content

As already stated, Tverdovskii and his colleagues estimated changes of hydrogen content coulometrically from careful measurements of the anodizing current up to a point where the electrode assumes very high positive values which suggests that all of the absorbed hydrogen had been removed. An analogous technique has also been applied recently by Makrides (1964) and Bucur (1965). One source of error in this general method is that all of the anodic species discharged electrolytically may not be utilized to reduce hydrogen, particularly in the later stages of removal when the hydrogen content of the surface is relatively low; and also when there is relatively slow diffusion of hydrogen in the solids—such as in alloys with higher contents of silver (Carson, to be published). A further source of error is the possibility of concurrent spontaneous desorption of hydrogen as molecules from surfaces of high catalytic activity. This will be relatively more important at lower

(positive) values of electrode potential and, for example, at a zero potential with respect to a Pt/H_2 electrode, it is equivalent to current densities of $\sim$ 3mA cm^{-2} in well-stirred solutions (Green and Lewis, 1964).

Changes of hydrogen content also have been estimated from conjoint measurements of relative electrical resistance (R/R_0)—provided relationships between H/Me and R/R_0 have previously been established for the particular alloy.

Finally, provided the rate–controlling step in the absorption of hydrogen from hydrogen-saturated solutions is the transport of dissolved molecules through the Brünner–Nernst layer, then changes of hydrogen content can be calculated by integration of the function k_0 $(P-p)$dt (Barton *et al.*, 1966a) where k_0 is the rate constant and p and P, respectively, are the vapour pressure of the hydride and the pressure under which the hydrogen gas is dissolved.

H. Estimations of Changes of Hydrogen Content During Desorption

In addition to the coulometric measurements of Tverdorskii and his colleagues, gradual changes of hydrogen content during the desorption of hydrogen from highly catalytically-active electrodes have again been calculated by integrations of the equation k_0 $(P-p)$dt following the introduction of additional hydrogen by cathodization after equilibration of the electrodes in hydrogen-saturated solutions, as well as by integration of the equation $k_0p$dt after transfer of hydrided specimens to solutions saturated with an inert gas such as argon, and stirred at a constant rate (Barton *et al.*, 1966a; Green and Lewis, 1966b). Changes of electrical resistance can also be employed to derive (or at least to provide a check on) changes of H/Me during removal of hydrogen, where '*desorption*" relationships between R/R_0 and hydrogen content have been derived in separate experiments (Barton *et al.*, 1966a).

I. Comparison of p–C–T Relationships for the Various Alloy Systems

In principle, the calculation of equilibrium pressures from electrode potential measurements requires that the hydrogen content at the surface does not exceed the composition of the bulk (except over regions where a phase transformation is taking place, and here the surface composition should remain constant over the course of the transformation). For these conditions to apply, the hydrogen must be able to dis-

perse itself throughout the solid by diffusion at a fast rate compared with that at which it is being added to or removed from the surface so that there is a minimal diffusion gradient existing within the specimen. This generally requires the values of diffusion coefficient, D, to be high (see Chapter 7). In practice, however, the value of D over a range of alloy compositions may decrease so sufficiently as to give rise to seriously enhanced experimental limitations under a particular set of conditions. Thus, for example, in recent studies with a series of Pd/Ag alloys (Carson, to be published) it has been found, using rates of absorption of $\sim$ 3 mA cm^{-2}, that for alloys containing $>$ 45% Ag the surface concentration of hydrogen can build up to values which can quite substantially exceed the true equilibrium value equivalent to the measured value of electrode potential. It has been found, in particular, that because of this, a potential plateau at $\sim$ 6 mV at 25° for 50% Ag alloys, which was suggested as a possibility from the form of preliminary results by Lewis and Schurter (1960), has turned out to be an experimental artifact. In principle, however, this type of problem can be overcome by decreasing the rate of absorption. For instance, under conditions where hydrogen is being absorbed from hydrogen-saturated aqueous solutions, the concentration of dissolved hydrogen gas can be reduced by "diluting" the solution with argon or with helium as carried out by Maeland and Flanagan (1965) in work with Pd/Au alloys.

Moreover, for lower ranges of content of alloying metal this does not appear to have been a serious source of error in deriving p–C relationships from measurements of changes of electrode potential during increases of H/Me in solutions saturated with hydrogen at atmospheric pressure. In the particular case of the Pd/Ag/H system where it is possible to compare relationships derived from electrode potential measurements recorded under these conditions with p–C relationships obtained by direct equilibration with hydrogen gas by Brodowsky and Poeschel (1965), as shown in Fig. 6.4, there is found to be good agreement for alloys with $\leqslant$ 40% Ag (Carson, to be published). It is necessary to draw attention to a further correction which it has been required to make to the preliminary communication of Lewis and Schurter (1960). This is, that in the case of the 40% Ag an apparent potential plateau with a value of $\sim$ 3 mV at 25° has latterly also been found to be an erroneous result (Carson and Lewis, 1966). The reason in this case was that the 40% Ag alloy available to Schurter had an inhomogeneous distribution of palladium and silver. The p–C relationships which I derived from the results with this 40% Ag alloy and published in diagrammatic form in a review article (Lewis 1960, 1961a) must also, therefore, be discounted.

Apart from the Pd/Ag/H system, p–C isotherms at close to 25° have not as yet been determined by direct equilibration for any other series of alloys, and relationships derived from electrode potential measurements represent the only source so far available from which to discern even overall trends of the relationships in these cases.

With general regard to the derived relationships which are available, there is overall agreement between the trends of results obtained by Tverdovskii and his colleagues [including those obtained by Vert and Tverdovskii (1954) for the Pd/Ag/H system] and the later results obtained with solid wires and sheets for the same systems, although there are certain differences of exact detail which are rather difficult to compare because only limited features of Tverdovskii's relationships are presented in tabular form.

It should also be mentioned here that in addition to those recent studies in the 1960s already cited in which changes of electrode potential have been measured over substantial ranges of hydrogen content, values

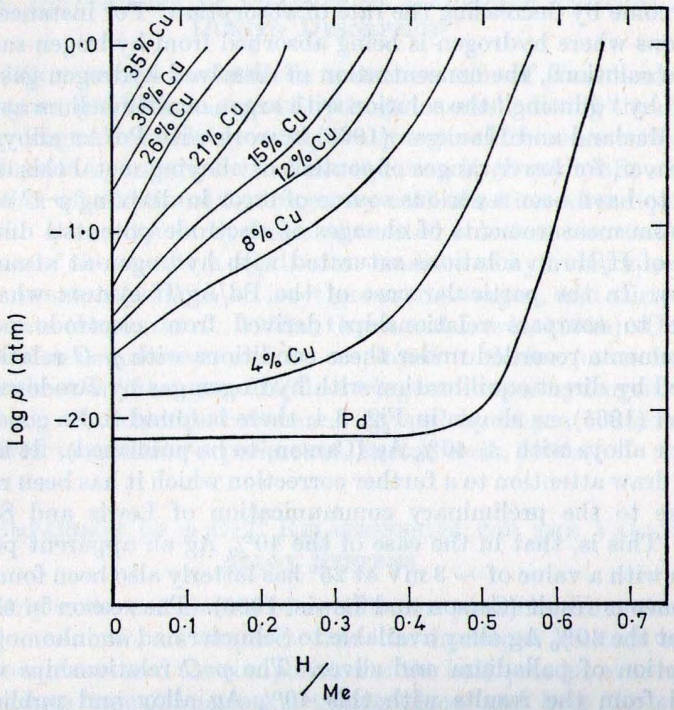


FIG. 6.6 Log p–C relationships for copper/palladium alloys derived from electrode potential measurements (at 24°) using alloys prepared by electrolytic co-deposition—after Karpova and Tverdovskii (1959).

of the electrode potential which it now seems probably correspond with the potential (E α, β) over regions of α- and β-phase co-existence, have also been recorded by Schuldiner, Hoare and Castellan with alloys in the form of wires and foils for the Pd/Au/H (Hoare *et al.*, 1958); Pd/Ni/H (Hoare and Schuldiner, 1958) and Pd/Rh/H (Hoare, 1960b) systems. The values obtained for Pd/Ni and Pd/Rh alloys are in fair agreement with later results of Barton *et al.* (1966a) and Green and Lewis (1966b). Possible reasons for differences in details are discussed in the later papers. In the case of the Pd/Au/H system, Hoare *et al.* (1958) have found that the potential of $E_{\alpha,\beta}$ stays almost constant over low contents of Au rather than exhibiting the smallish increases recorded by Maeland and Flanagan (1965).

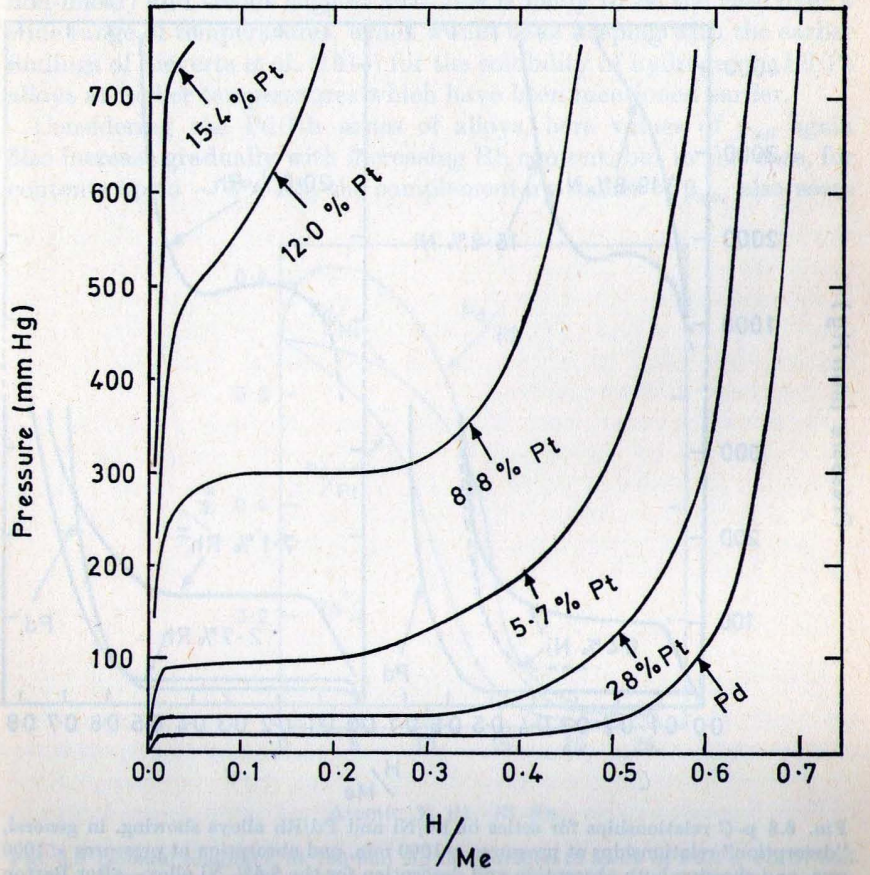


FIG. 6.7 p–C relationships for a series of Pd/Pt alloys at 25°—after Carson *et al.* (1960).

The increase of $E_{\alpha,\beta}$ found by Maeland and Flanagan would group the Pd/Au/H system with the Pd/Ag/H system in this respect. However, even the increases found by Maeland and Flanagan are substantially less marked than for the Pd/Ag/H system, and this seems to parallel the generally less marked maxima in relationships between gold content and hydrogen solubilities found earlier by Sieverts *et al.* (1915) at higher temperatures as previously discussed. Results for the Pd/Cu/H system have only been obtained for "alloys" formed by electrolytic co-deposition from mixtures of salts (Karpova and Tverdovskii, 1959). The form of the results shown in Fig. 6.6 indicates that at *ca* 25° successive isotherms fall wholly within one another which is in broad similarity with the Pd/Ni and Pd/Pt series discussed following.

In general, the Pd/Pt/H, Pd/Rh/H and Pd/Ni/H systems exhibit

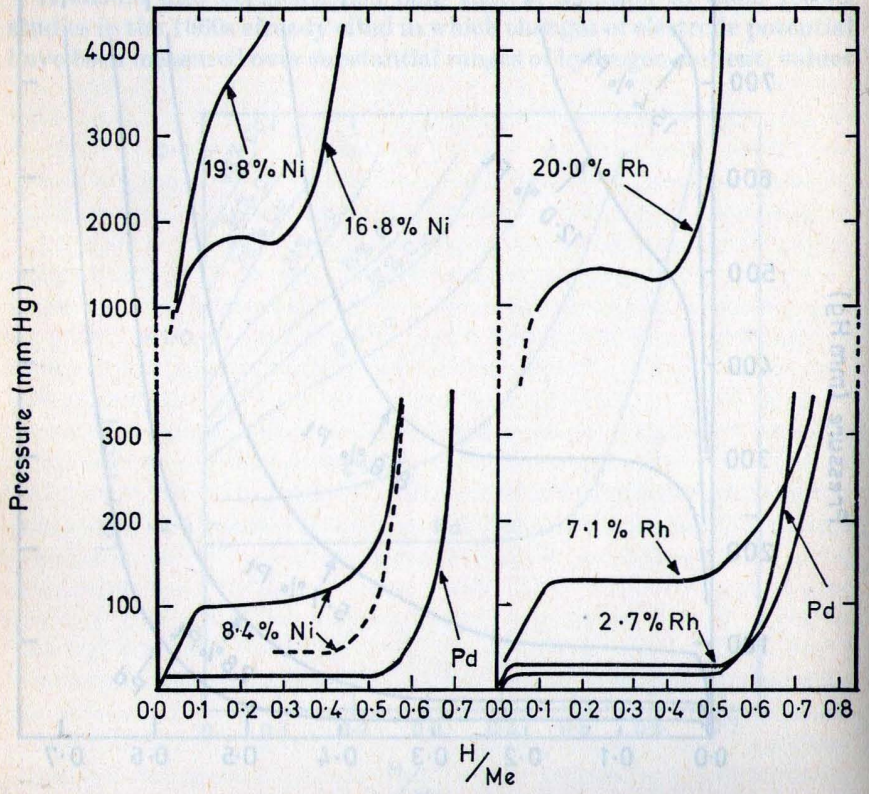


FIG. 6.8 *p–C* relationships for series of Pd/Ni and Pd/Rh alloys showing, in general, "desorption" relationships at pressures >1000 mm, and absorption at pressures <1000 mm, and showing both absorption and desorption for the 8·4% Ni alloy—after Barton *et al.* (1966a) and Green and Lewis (1966b).

quite close similarities of trends in their relationships as a function of the content of alloying metal. This is particularly the case for the Pd/Pt and Pd/Ni series of alloys. Here in both instances the value of the equilibrium vapour pressure $p_{\alpha,\beta}$ over regions of α- and β-phase co-existence shows a gradual increase with increasing contents of either Pt or Ni as shown in Figs 6.7 and 6.8. At the same time, there is in both cases a corresponding decrease of the range of hydrogen contents over which the plateau extends (i.e., a gradual decrease of β_{min}) so that plots of successive isotherms fall wholly within one another (Carson *et al.*, 1960; Barton *et al.*, 1966a; Green and Lewis, 1966b) over a range of temperature from 0 to 59°. As a result, solubilities always exhibit a decrease with increasing Ni or Pt content, no matter what pressures they are compared at (although the form can be markedly non-linear) and trends suggest that this is likely to be the case over a wide range of temperatures, which would be in keeping with the earlier findings of Sieverts *et al.* (1915) for the solubility of hydrogen in Pd/Pt alloys at higher temperatures which have been mentioned earlier.

Considering the Pd/Rh series of alloys, here values of $p_{\alpha,\beta}$ again also increase gradually with increasing Rh content, but in this case, for contents up to ~ 3% Rh, the complementary values of β_{min} also seem

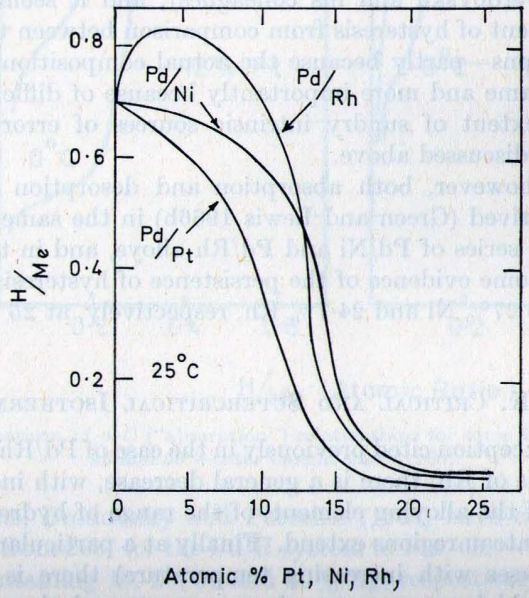


FIG. 6.9 Isobaric solubility, at 760 mm Hg of hydrogen in series of Pd/Pt, Pd/Ni and Pd/Rh alloys at 25°—after Carson *et al.* (1960), Barton *et al.* (1966a).

to exhibit an increase. Because of this, plots against Rh content of the solubilities of hydrogen under a pressure of ~ 1 atm exhibit a maximum at ~ 3% Rh (Tverdovskii and Stetsenko, 1952; Green and Lewis, 1966b) as illustrated in Fig. 6.9. This maximum, however, gradually disappears when comparisons are made at lower pressures—which is to some extent a reversal of the analogous sequence of changes of this form of comparison of solubilities in the case of the Pd/Ag/H system.

J. Hysteresis of p–C–T Relationships

The observations of Brodowsky and Poeschel (1965) of hysteresis between the absorption and desorption relationships over regions where the α- → β-phase and β- → α-phase transformations occurred in the Pd/Ag/H systems, has gained confirmation from relationships derived from electrode potential measurements which provide evidence of hysteresis for alloys with contents of up to ~ 20% Ag (A. W. Carson, unpublished).

Until very recently, the relationships obtained for other alloy systems either have been derived only during absorption (as in the more recent studies with pre-melted alloys) or only during desorption (as in the studies of Tverdovskii and his colleagues); and it seems difficult to assess the extent of hysteresis from comparison between the two types of investigations—partly because the actual compositions were rarely exactly the same and more importantly because of difficulties of estimating the extent of sundry intrinsic sources of error which have already been discussed above.

Recently, however, both absorption and desorption relationships have been derived (Green and Lewis 1966b) in the same series of experiments for series of Pd/Ni and Pd/Rh alloys, and in these systems there is still some evidence of the persistence of hysteresis at compositions of up to 27% Ni and 24·7% Rh, respectively, at 25°.

K. Critical and Supercritical Isotherms

With the exception cited previously in the case of Pd/Rh alloys at low concentrations of Rh, there is a general decrease, with increasing concentrations of the alloying element, of the range of hydrogen contents over which plateau regions extend. Finally at a particular composition (which decreases with increasing temperature) there is no longer a region over which pressure remains constant, and the p–C relationships have the appearance of a critical isotherm. The isotherms for

alloys with still higher contents of alloying metals should then be supercritical in form. A concise summary of these changes is that the critical temperature decreases with increasing content of alloying metal as, for example, may be deduced from comparison of the p–C relationships of certain Pd/Pt alloys shown in Fig. 6.10. From thermodynamic

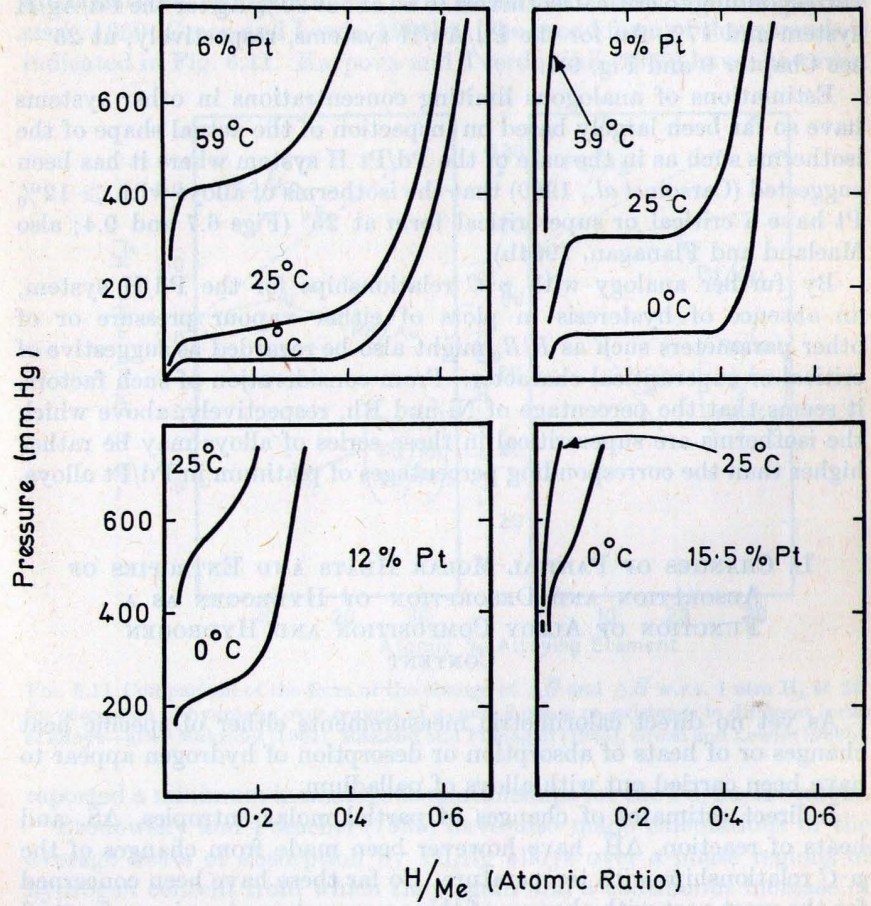


Fig. 6.10 Comparison of p–C ("absorption") relationships for some Pd/Pt alloys at 0, 25 and 59°—after Carson *et al.* (1960).

considerations, Brodowsky and Poeschel (1965) have calculated that T_c decreases from 295° for the Pd/H system to 144, 63, −91 and −219° for alloys containing 10, 20, 30 and 40% Ag, respectively.

An alternative method of estimating the composition for a particular system which would correspond with a critical isotherm, is to plot

alloy composition against the values of the X-ray parameters corresponding to α_{max} and β_{min} at a given temperature and to find by extrapolation the compositions when the values of these two parameters are coincident. From plots of this type, Axelrod and Makrides (1964) and Maeland and Flanagan (1965) have estimated the compositions corresponding to critical isotherms to be about 30% Ag for the Pd/Ag/H system and 17% Au for the Pd/Au/H systems, respectively, at 25°—see Chapter 9 and Fig. 9.4.

Estimations of analogous limiting concentrations in other systems have so far been largely based on inspection of the actual shape of the isotherms such as in the case of the Pd/Pt H system where it has been suggested (Carson *et al.*, 1960) that the isotherms of alloys with $\geqslant$ 12% Pt have a critical or supercritical form at 25° (Figs 6.7 and 9.4; also Maeland and Flanagan, 1964b).

By further analogy with p–C relationships for the Pd/H system, an absence of hysteresis in plots of either vapour pressure or of other parameters such as R/R_0 might also be regarded as suggestive of critical or supercritical character. From consideration of such factors, it seems that the percentage of Ni and Rh, respectively, above which the isotherms are supercritical in these series of alloys may be rather higher than the corresponding percentages of platinum in Pd/Pt alloys.

L. Changes of Partial Molar Heats and Entropies of Absorption and Desorption of Hydrogen as a Function of Alloy Composition and Hydrogen Content

As yet no direct calorimetric measurements either of specific heat changes or of heats of absorption or desorption of hydrogen appear to have been carried out with alloys of palladium.

Indirect estimates of changes of partial molar entropies, $\Delta\bar{S}$, and heats of reaction, $\Delta\bar{H}$, have however been made from changes of the p–C relationships with temperature. So far these have been concerned for the most part with changes of these parameters at regions of α- and β-phase co-existence as a function of alloy composition. They have been derived from the temperature dependence of the partial molar free energy change $\Delta\bar{G}_{\alpha,\beta\,(\beta,\alpha)}$ calculated as $RT \ln p_{\alpha,\beta\,(\beta,\alpha)}$. Results suggest that for all the alloys so far studied, the corresponding entropy changes $|\Delta\bar{S}_{\alpha,\beta\,(\beta,\alpha)}|$ remain fairly constant at about 20–25 Kcal mole^{-1} deg^{-1} H_2 (Carson *et al.*, 1960; Maeland and Flanagan, 1965; Green and Lewis, 1966b). As a result the trends of changes of $|\Delta\bar{H}_{\alpha,\beta\,(\beta,\alpha)}|$ are broadly

similar to changes of $p_{\alpha,\beta}$ in that there is a gradual increase in the case of the Pd/Ag/H and Pd/Au/H systems as a function of silver and gold contents, respectively (Tverdovskii *et al.*, 1959b; Makrides, 1964; Maeland and Flanagan, 1965)—whilst for the Pd/Pt/H, Pd/Rh/H and Pd/Ni/H systems there is an analogous continuous decrease which is quantitatively quite similar in form for all three series of alloys (Carson *et al.*, 1960; Green and Lewis, 1966b). The broad form of these trends is indicated in Fig. 6.11. Karpova and Tverdovskii (1959) have, however,

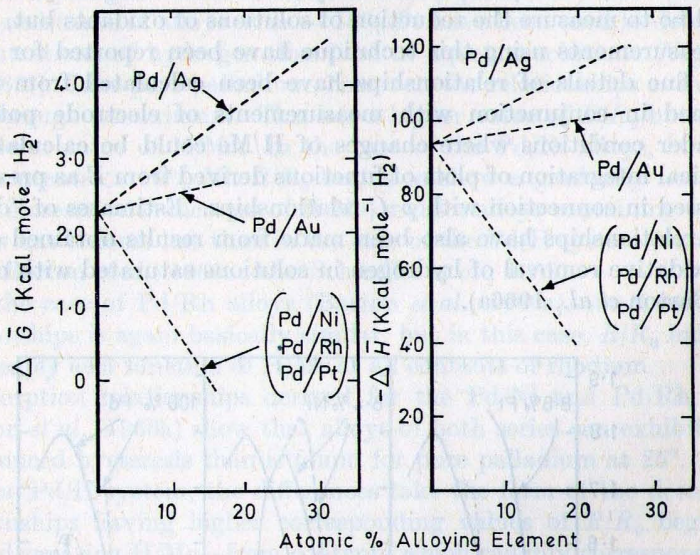


FIG. 6.11 Comparison of the form of the change of $\Delta\bar{G}$ and $\Delta\bar{H}$ w.r.t. 1 atm H_2 at 25° for *absorption* of hydrogen over regions of α- and β-phase co-existence in different series of alloys—after Makrides (1964), Maeland and Flanagan (1965), Green and Lewis (1966b).

reported a minimum in analogous relationships for the Pd/Cu/H system.

Brodowsky and Poeschel (1965) have also made calculations of the average heats of absorption by Pd/Ag alloys over α-phase regions of hydrogen content from which they again find a continuous increase of $|\Delta\bar{H}|$ with increasing silver content up to 40% Ag. Finally, Simons and Flanagan (1965a) have recently reported that they have calculated that $|\Delta\bar{H}|$ exhibits significant increases with increasing hydrogen content in the case of some Pd/Au alloys of a so far unspecified composition.

M. Relationships Between Hydrogen Content and Electrical Resistance

To derive relationships between these two parameters at near to room temperature, one method which has been quite widely employed to measure H/Me at a particular value of R/R_0 has been to outgas the specimen *in vacuo* immediately after R/R_0 had been recorded *in situ* (Rosenhall, 1935; Carson *et al.*, 1960; Maeland and Flanagan, 1965; Barton *et al.*, 1966a). One relatively convenient alternative method would be to measure the reduction of solutions of oxidants but, so far, no measurements using this technique have been reported for alloys. Some fine details of relationships have been calculated from results obtained in conjunction with measurements of electrode potential, E, under conditions where changes of H/Me could be calculated by graphical integration of plots of functions derived from E as previously discussed in connection with p–C relationships. Estimates of "desorption" relationships have also been made from results obtained during the oxidative removal of hydrogen in solutions saturated with oxygen gas (Barton *et al.*, 1966a).

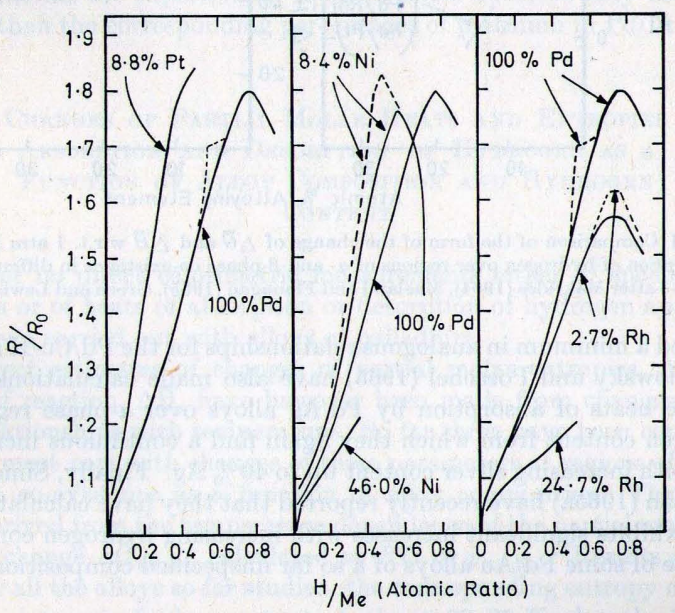


Fig. 6.12 Relationships between relative electrical resistance and hydrogen content for certain alloys of the Pd/Pt, Pd/Ni and Pd/Rh series; "desorption" relationships are shown by broken lines—after Carson *et al.* (1960), Barton *et al.* (1966a).

As in the case of the p–C–T relationships, the Pd/Pt, Pd/Ni and Pd/Rh series of alloys exhibit relatively uncomplicated sequences of changes in the form of the relationships from those for pure palladium (see Chapter 5).

As illustrated for certain examples in Fig. 6.12, with increasing contents of alloying element at relatively low contents of Ni and Pt, both the Pd/Ni and Pd/Pt series of alloys initially exhibit a gradually steeper increase of R/R_0 with increasing hydrogen content over much of the range of hydrogen contents where α- and β-phases co-exist. [Changes of the resistance of alloys with ~ 15% Pt have been used to determine concentrations of hydrogen dissolved in aqueous solutions (Vignet *et al.*, 1963)]. Like pure palladium, however, the relationships eventually pass through a maximum. This has a higher value of R/R_0 but occurs at a lower value of H/Me. In the case of the Pd/Ni alloys, however, with contents > 10% Ni, R/R_0 begins to show a gradually less steep initial increase with increase of H/Me, and for alloys containing ~ 20% Ni this has become less than in the case of the Pd/H system (van Loef, 1963; Barton *et al.*, 1966a; also Schindler *et al.*, 1959).

In the case of Pd/Rh alloys (Barton *et al.*, 1966a), the form of the relationships is again basically similar, but in this case, R/R_0 increases less steeply as a function of H/Me at all contents of rhodium.

Desorption relationships derived for the Pd/Ni and Pd/Rh alloys (Barton *et al.*, 1966a) show that alloys of both series can exhibit more pronounced hysteresis than is found for pure palladium at 25°. Again like the Pd/H system, the differences take the form of the desorption relationships having higher corresponding values of R/R_0 beginning —for decreasing H/Me—from contents which roughly correspond with the onset of the β- → α-phase transformation. In the desorption relationships of some of the alloys, R/R_0 can then pass through maximum values which may be markedly higher than those of the corresponding absorption relationship (Barton *et al.*, 1966a) which is an effect obtained in the case of the Pd/H system at temperatures of 160–200° (see Chapter 4).

The Pd/Ag/H system has been investigated over an even somewhat wider range of compositions. Moreover, generally good agreement has been found between relationships derived at near room temperature in different studies (Rosenhall, 1935; Carson, to be published). Figure 6.13 illustrates that with increasing contents of Ag, successive alloys show less steep rises of R/R_0 with H/Me at 25°. Perhaps one point of particular interest in the relationship for the 10% Ag alloy is that rather sharp changes of the slope of the relationships seem, from comparison with the corresponding p–C relationships, to correspond with both the onset

and the completion, respectively, of the α- → β-phase transformation—the latter point being much more sharply defined than in the case of the Pd/H system. Clear evidence of hysteresis between absorption and

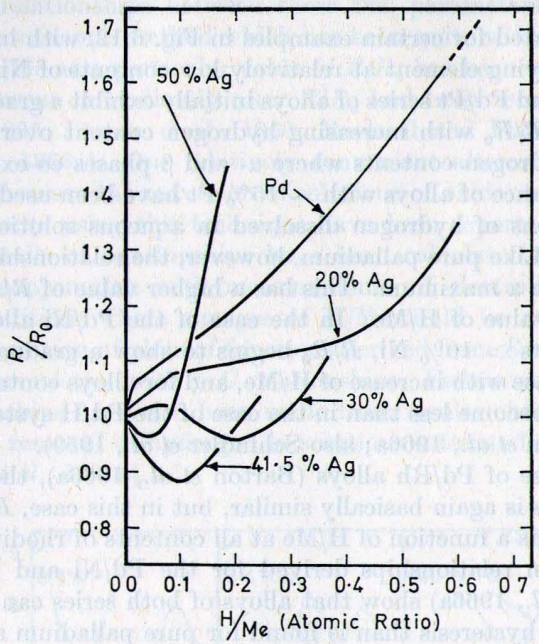


FIG. 6.13 Comparison of changes in the form of relationships between R/R_0 and hydrogen content for sundry Pd/Ag alloys—after measurements of Rosenhall (1935).

desorption relationships has only been found for alloys with 10 and 20% Ag (Carson to be published).

For alloys with contents of ~ 40% Ag, Fig. 6.13 shows that R/R_0 can actually exhibit a decrease over a middle range of hydrogen contents where p–C relationships suggest there are regions of quasi phase transitions even when extrapolations of plots of X-ray parameters suggest the isotherms would have a supercritical form. At still higher contents of 50 and 60% Ag, however, the relationships again exhibit an approximately linear increase of R/R_0 except at very low values of H/Me—and this could perhaps be correlated with a continuous foreshortening of this quasi transition region. Relationships have also been derived at higher temperatures by direct equilibration of the specimens with hydrogen gas at temperatures within the range 155–484° by Sieverts and Hagen (1935), and in general these exhibit a broadly similar sequence of changes to those in Fig. 6.13, as illustrated by results obtained at 155° plotted in their Fig. 10. Sieverts and Hagen

also obtained some relationships for the Pd/Au/H system with three alloys containing 18·8, 26·5 and 35·1 atomic percent Au and these seem to show a somewhat analogous sequence of changes of the form of the relationships with increasing contents of gold to the Pd/Ag series.

N. Changes of the Temperature Coefficient of Electrical Resistance With Changes of Hydrogen Content

In general, the temperature coefficients of electrical resistance, α, of the hydrogen-free alloys gradually decrease over the ranges of concentration of alloying element where the specific electrical resistance shows an increase (Vines and Wise, 1941). The trend of changes of α with increases of hydrogen content is broadly the same as this in that similarly to findings for pure palladium, α shows a gradual decrease (except possibly over α-phase regions) over regions where R/R_0 is an increasing function of hydrogen content. Specific examples of this are provided by results obtained for series of Pd/Ni and Pd/Rh alloys (Barton *et al.*, 1966a). Alloys of the Pd/Ag series present an interesting extension of this general trend in that for those alloys (~ 40% Ag) which exhibit decreases of R/R_0 over middle ranges of hydrogen content there is evidence of a parallel *increase* of α (Carson, to be published).

CHAPTER 7

Diffusion of Hydrogen Through Palladium and Palladium Alloys

A. General Introduction and Discussion of Uses of Palladium Membranes

In terms of practical utility, hydrogen is most often associated with palladium because of the widespread use of the metal as a membrane (or septum) which permits a rapid rate of permeation of hydrogen and provides a convenient method of separating it out of gaseous mixtures.

For some time, this general method of hydrogen purification was largely confined to relatively small scale research studies, but latterly it seems to have assumed an increasing industrial importance—although it is now alloys of palladium which are usually employed rather than the pure metal (Darling, 1963; Read and Glascock, 1966).

Again, comparatively recently, there has been a related interest in the use of palladium or palladium alloys as the anodes or "hydrogen electrodes" in fuel cells. Here the membrane separates gaseous and liquid phases. The hydrogen enters from the gas side where it may have been formed by a cracking process from methanol or hydrocarbons (Vertes and Hartner, 1965) and after diffusion through the membrane it is electrochemically oxidized at the "diffusion" interface with the electrolyte, (see Busson *et al.*, 1963; von Sturm and Kohlmüller, 1965; Cleary and Greene, 1965). The reverse of this process where hydrogen is *generated* at the electrolyte side and is *evolved* at the gaseous interface, also has been suggested as a smaller scale method for producing very pure hydrogen without using gas cylinders (Darling, 1963; Jacobsen, 1965).

The rate of diffusion of hydrogen through the actual solid membrane will be governed by the diffusion coefficient, D, appropriate to its chemical composition (i.e., in the case of palladium whether this is either α- or β-phase) and to the concentration gradient across the membrane and to its thickness.

In addition, however, the overall rate of permeation also is dependent on the catalytic efficiency of the intermediate reaction steps on the

surfaces of exit and entry, and also on the transport of reactants and products up to and away from these surfaces. In particular, conditions can quite frequently arise where one or other of these steps may be rate-determining, i.e., proceeding more slowly than the diffusion of hydrogen through the solid (Castellan, 1964).

Next it seems worthwhile to briefly introduce the simplest diffusion relationships which might be expected to apply when diffusion through the hydrided palladium is indeed the slowest stage.

B. General Formulation of Diffusion Equations Based on Fick's First Law

Provided transport of hydrogen through the solid palladium governs the rate of permeation, and further provided that there are no sharp discontinuities of composition in the solid (such as a boundary between regions of α- and β-phases) the rate of permeation, P, can be written in terms of Fick's first law as:

$$P = D\frac{(C_{\text{entry}} - C_{\text{exit}})}{\delta} \tag{7.1}$$

where $D(\text{cm}^2\ \text{sec}^{-1})$ is the diffusion coefficient for the particular phase, δ is the thickness of the membrane and C_{entry} and C_{exit} are the concentrations of hydrogen dissolved in the membrane at the interfaces of entry and exit, respectively.

Then with δ expressed in cm and the concentrations of hydrogen in the solid expressed as relative volumes (i.e. $cc\text{H}_2/cc\text{Pd}$—cf. Table 2.2) the permeation rates are obtained as $cc\text{H}_2/\text{cm}^2/\text{cm}$.

Considering Eq. 7.1, it is clear that when comparing rates of permeation through membranes of different metals—all of which have a common cross-sectional area and common thickness δ—fast "rates" of permeation can result from high values of the concentration gradient as well as from high values of D on which attention is more usually centred.

C. Expressing Fick's Equation in Terms of Pressure

Relationships between permeation rates and diffusion constants often have been written in terms of gas pressures or powers of the gas pressure rather than in terms of concentrations. This is a more convenient form in which to obtain a permeation rate by insertion of experimentally determined values of pressure and perhaps it may also be the result of widespread interest in the interpretation of problems concerning the

relationships between diffusion rates and pressures at very low pressures. However, from the viewpoint of those not well versed in diffusion problems it rather directs attention away from the fact that the critical variable is the solubility of gas in the solid as a function of pressure.

In practice, experimental results show that over wide ranges of pressure the solubility of hydrogen in nickel or platinum is approximately directly proportional to the square root of pressure, i.e.,

$$C = kp^{\frac{1}{2}} \tag{7.2}$$

A similar approximation, with characteristic values of k, is found to hold fairly well (Chapter 2) for the relationship between pressure and the solubility of hydrogen in the α-phase of the Pd/H system. Substitution for C in Eq. 7.1. gives

$$P = kD\frac{(p^{\frac{1}{2}}_{\text{entry}} - p^{\frac{1}{2}}_{\text{exit}})}{\delta} \tag{7.3}$$

Better approximations of the correct concentration have been suggested to be given by equating concentration (hydrogen content) to alternative powers of pressure, leading to a more generalized relationship

$$P = kD\frac{(p^{n}_{\text{entry}} - p^{n}_{\text{exit}})}{\delta} \tag{7.4}$$

where values of $n = 0{\cdot}8$ or $0{\cdot}68$ have recently been proposed at particular temperatures and ranges of pressure (De Rosset, 1960; Hurlbert and Konecny, 1961). In general, values of n are obtained from plots of log P against log p.

Nevertheless, these equations still represent only approximations to provide a tidy simplified formulae and are less accurate than an experimental measurement of the corresponding value of solubility for each value of pressure. In the case of the Pd/H system, such correlations can be provided from p–C–T data over a wider range of temperature and pressure as surveyed in Chapter 2.

D. Some General Comments on the Influence of Surface Processes on Permeation Rates

In deriving diffusion coefficients from permeation rates by means of the Fick first law equation, it has to be assumed that equilibration between gas and solid is complete and rapid at both the entry and exit surfaces, so that it is diffusion through the solid which is the slow and rate-determining step, and so that the concentrations of hydrogen at the

surfaces may be derived from the gas pressures through p–C–T relationships. However, there is a good deal of evidence that this has often not been the case in experimental studies. For instance, there have been a number of reports of irreproducibility of the permeation rates obtained with different membranes of identical dimensions, and the rate of permeation has often been found to slow down during experiments with a particular membrane (Jewett and Makrides, 1965) although this may have been the result of inadequate circulation of gas (see the following).

E. Limiting Lower Temperatures for Rapid Rates of Permeation: Various Methods of Pre-activation of Surfaces

In general, the surfaces of palladium membranes do not readily equilibrate with molecular hydrogen at room temperature. Recently, however, some success in this respect has been achieved by various activation procedures, such as by plating on a layer of palladium black (Küssner, 1962; Wicke and Bohmholdt, 1964; Jewett and Makrides, 1965); bombardment by argon ions formed in low pressure gaseous discharges (Jewett and Makrides, 1965; also Ulbrich, 1939; Norberg, 1952); or by contacting the surfaces with materials such as copper (Wicke and Nernst, 1964; Brodowsky and Poeschel, 1965) or hydrides of uranium and tantalum (Küssner and Wicke, 1960) which were believed to be more efficient than palladium for dissociating molecular hydrogen and from which the dissociated atoms migrate to the palladium surface.

Nevertheless, up to the present most studies of permeation rates have been carried out at temperatures exceeding 250°, and even at such high temperatures the specimens may need to be heated in oxygen for a period (Hurlbert and Konecny, 1961; Simons and Flanagan, 1965a; Jewett and Makrides, 1965) before reproducibly high rates of permeation are recorded.

F. Chemical Poisoning of the Diffusion Process

Even at temperatures exceeding 250°, marked decreases of permeation rates (sometimes accompanied by embrittlement, and finally cracking) have been caused by exposure to mercury vapour or to compounds containing sulphur, arsenic and related elements (Connor, 1962; Darling, 1964b) or to bromine and iodine (Barton *et al.*, 1963b). Certain unsaturated hydrocarbon vapours may also have a temporary poisoning

effect (Darling, 1964b) and Hurlbert and Konecny (1961) have suggested that zinc distilled from hard solder could have acted as a poison in the measurements of Silberg and Bachman (1958) which seems the only fairly recent study in which permeation rates could not be obtained which were inversely proportional to the thickness of the membrane. At present, it seems generally accepted that the poisoning can be accounted for either in terms of inhibition of the dissociation of hydrogen molecules to chemisorbed atoms or by the poisoning element (e.g., arsenic) forming a layer of a fairly high melting compound within which there is a low solubility of hydrogen and/or a high diffusion coefficient.

G. Adequate Gas Circulation: Bleed Rates

Experimental work by Darling (1958) has shown the necessity for maintaining movement and circulation of the gas at the input or upstream side of the membrane. Without such circulation, permeation rates have been found to decrease to negligibly low values as indicated by the results in Fig. 7.1. Darling has suggested that this apparent loss

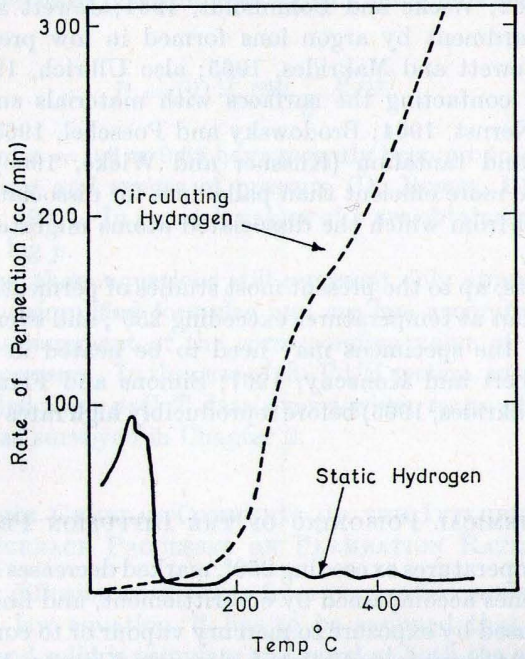


Fig. 7.1 Examples of permeabilities of a palladium tube when the gas at the high pressure (upstream) side is kept either static or in circulation by bleeding away some of the gas—after Darling (1958).

of permeability is primarily due to the development of a stagnant layer of impurities adjacent to the surface. Darling's observations have been broadly confirmed by other recent work of Hurlbert and Konecny (1961) and of de Rosset (1960). All three studies are in agreement that this effect can be prevented by bleeding away quite a small fraction of the input gas in order to remove such stagnant impurities and cause gentle stirring. When this is carried out excellent reproducibility of results has been obtained and permeation rates were maintained constant for prolonged periods even when the sources of hydrogen was provided by commercial cylinders without further purification. Such a "bleed" arrangement is generally a standard feature of commercial models of hydrogen purifier.

H. Some Methods of Measurement of Permeation Rates

In the majority of measurements of steady-state permeation rates, the specimen has either been in the form of a tube sealed at one end as in Graham's original measurements, or in the form of a sheet of foil, of which a wire as employed in the experiments of Toda (1958) may be considered an extreme case. Examples of experimental arrangements incorporating specimens in either of these forms are shown in Figs 7.2 and 7.3. In perhaps the majority of practical experimental set ups, the membrane has been employed in the form of a tube or bulb. For joining into a particular apparatus, the tube generally is soldered to copper which has been sealed into borosilicate glass; or else it can be welded to platinum which forms a good seal to soda glass.

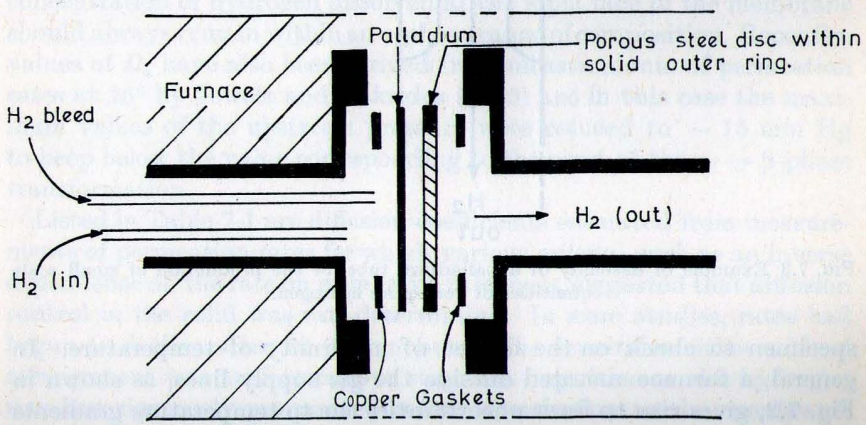


Fig. 7.2 Example of assembly of a palladium disc for measurements of permeation rates and diffusion constants—after Hurlbert and Konecny (1961).

Temperature generally has been recorded by thermocouples located close to the specimen and in the case of palladium tubes, arrangements can be made to move the tip of the thermocouple along the length of the

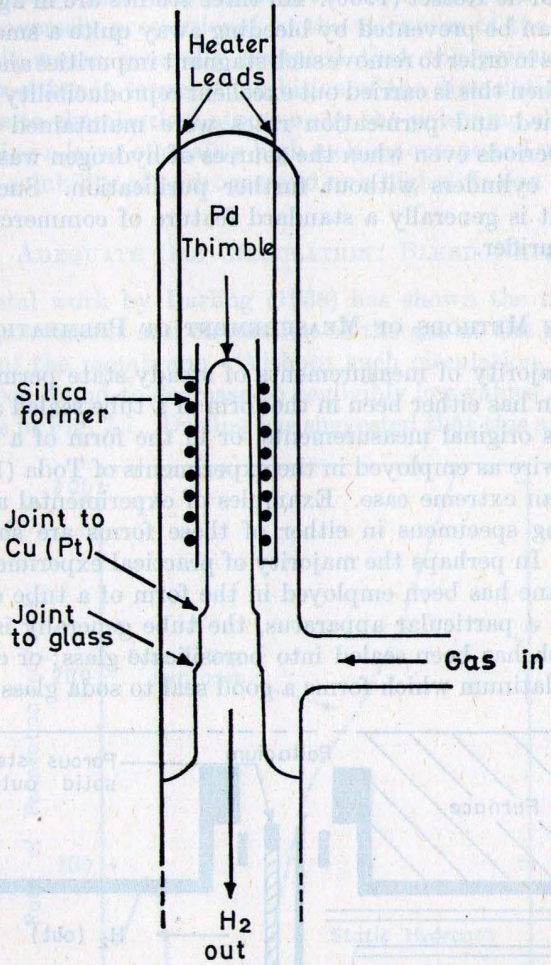


FIG. 7.3 Example of assembly of a palladium tube for the production of small scale quantities of very pure hydrogen.

specimen to check on the degree of uniformity of temperature. In general, a furnace mounted outside the gas supply lines, as shown in Fig. 7.2, gives rise to fewer uncertainties due to temperature gradients along the specimen. By connecting current leads directly to it, the specimen also has been heated by being used itself directly as an ele-

ment. However, having the heater wound on a former (often silica), as shown in Fig. 7.3, is often convenient, and although this arrangement may not be ideal for absolute measurements of permeation rates and diffusion constants, it has been employed for delivering controlled amounts of hydrogen in a number of experimental studies.

The actual rates of permeation generally have been measured either by means of flow meters placed in the high pressure or upstream side of the membrane when exactly true steady-state conditions apply or, alternatively, by measuring rates of increase of pressure on the low pressure side—generally when the gas is permeating into a previously evacuated volume on the low pressure side (Toda, 1958; Katz and Gulbransen, 1960).

I. Calculation of α-phase Diffusion Coefficients (D_α) from Studies Involving Only Gas/Solid Interfaces

Because of the general difficulty in achieving rapid equilibrium between the surface of membranes and hydrogen gas at temperatures below *ca* 200°, the majority of studies of steady-state permeation rates have been carried out within a range of temperatures from 200 to 600°.

Although recently in studies by de Rosset (1960) and by Hurlbert and Konecny (1961) the maximum pressures employed have been extended to ~ 46 and ~ 7 atm, respectively, in most studies the pressure of gas at the input (or upstream) side has been less than or roughly equal to 1 atm. Consideration of p–C relationships (see Chapter 2) indicates that within these ranges of temperature and pressure, the concentration of hydrogen dissolved at the input face of the membrane should always remain within an α-phase range of composition. Recently, values of D_α have also been derived from measurements of permeation rates at 25° by Jewett and Makrides (1965) and in this case the maximum values of the upstream pressure were reduced to ~ 15 mm Hg to keep below the value corresponding to the onset of the α- → β-phase transformation.

Listed in Table 7.1 are diffusion coefficients estimated from measurements of permeation rates for which various criteria, such as an inverse dependence of the rate on membrane thickness, suggested that diffusion control in the solid was rate-determining. In some studies, rates had begun to decline after 10–30 min but in the remainder either a bleed arrangement was used to remove stagnant impurities or else hydrogen was first rigorously pre-purified before introduction to the membrane. In general, results in Table 7.1 seem reasonably interconsistent within a factor of about 2. In those cases where authors had merely recorded

TABLE 7.1

Comparison of some measurements of the diffusion coefficient for hydrogen in α-phase regions

Temperature °	D_α(cm² sec⁻¹)	Technique	Reference
25	$1{\cdot}6 \times 10^{-7}$	A	i
182	$1{\cdot}05$–$1{\cdot}48 \times 10^{-5}$	C	a
200	$8{\cdot}9 \times 10^{-6}$	A	d
213	$1{\cdot}3 \times 10^{-5}$	A	g
240	$2{\cdot}16$–$3{\cdot}16 \times 10^{-5}$	C	a
260	$3{\cdot}3 \times 10^{-5}$	B	e
266	$2{\cdot}3 \times 10^{-5}$	A	g
300	$2{\cdot}2 \times 10^{-5}$	A	d
ca 300	$3{\cdot}5 \times 10^{-5}$	B	c
301	$3{\cdot}0 \times 10^{-5}$	A	g
333	$4{\cdot}0 \times 10^{-5}$	A	b
ca 335	*ca* $6{\cdot}0 \times 10^{-5}$	B	c
343	$2{\cdot}9 \times 10^{-5}$	A	f
350	$5{\cdot}5$–$6{\cdot}7 \times 10^{-5}$	A	h
352	$4{\cdot}7 \times 10^{-5}$	A	g
379	$5{\cdot}6$–$5{\cdot}8 \times 10^{-5}$	A	g
399	$5{\cdot}2 \times 10^{-5}$	A	f
400	$6{\cdot}9 \times 10^{-5}$	A	b
400	$5{\cdot}15 \times 10^{-5}$	A	d
454	$7{\cdot}4 \times 10^{-5}$	A	f
500	$8{\cdot}4 \times 10^{-5}$	A	d
504	$1{\cdot}1 \times 10^{-4}$	A	b
600	$1{\cdot}3 \times 10^{-4}$	A	d
616	$1{\cdot}8 \times 10^{-4}$	A	b

A, Measurements of steady-state permeation rates; B, Estimated from plots of the time lag before the setting up of steady state rates; C, Calculated from the rate of permeation into a solid sphere.

(a) Jost and Widmann (1935); (b) Lombard *et al.* (1937); (c) Barrer (1940); (d) Darling (1958); (e) Toda (1958); (f) de Rosset (1960); (g) Katz and Gulbransen (1960); (h) Hurlbert and Konecny (1961); (i) Jewett and Makrides (1965), see, however, a proposed correction by Simons and Flanagan (1965a).

permeation rates rather than diffusion coefficients the latter were determined through Eq. 7.1, and the concentration gradients were estimated either directly or by interpolation of p–C relationships of Sieverts (1914); Sieverts and Zapf (1935); Gillespie and Galstaun (1936) and Sieverts and Danz (1937).

Two less direct methods have been employed for calculations of D_α. In the time-lag method first employed in the case of the Pd/H system by Barrer (1940), values of D_α can be derived from the time taken for the onset of steady-state rates of permeation after admission of hydrogen

to the upstream side of the membrane. Selected values from Barrer's results are given in Table 7.1 together with an additional determination at 260° by the same method obtained more recently by Toda (1958). Table 7.1 also includes results at two temperatures obtained by Jost and Widmann (1935, 1940) from measurements of the rate of absorption of hydrogen by spheres of palladium with surfaces which had been activated by a plating of palladium black.

J. MIGRATION OF HYDROGEN IN α-PHASE COMPOSITIONS IN AN ELECTRIC FIELD GRADIENT

In the series of experiments by Coehn and his collaborators (Coehn and Specht, 1930; Coehn and Jürgens, 1931; Coehn and Sperling, 1933) and also by Duhm (1935), studies were made of the migration of hydrogen in palladium under the influence of a voltage gradient created by the passage of an electric current. Results indicated that the hydrogen was transported preferentially towards the cathode, and this was interpreted as evidence that the absorbed hydrogen was in the form of protons. There seems a possibility that in some of Coehn's experiments the hydrogen might have been transported through solution contacting the surface rather than through the bulk lattice. Nevertheless, further evidence of protonic migration was also obtained in later experiments of Wagner and Heller (1940) (see also Jost, 1952) whose experimental

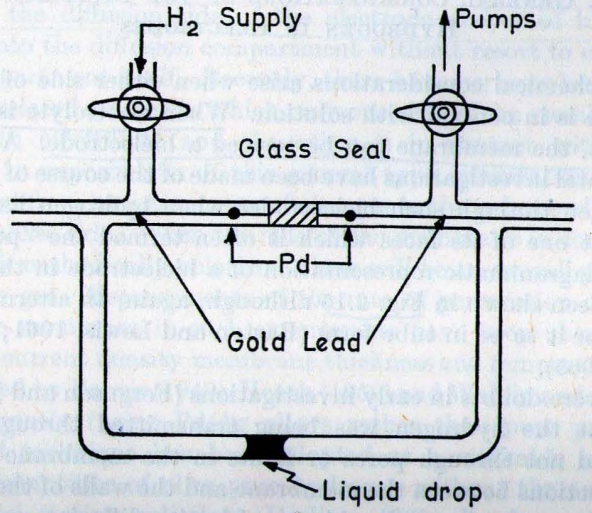


FIG. 7.4 Diagram of apparatus for measurements of permeation of hydrogen through palladium under the influence of an electric field—after Wagner and Heller (1940).

arrangement is diagrammatically illustrated in Fig. 7.4. Here transport numbers for the migration of hydrogen under a voltage gradient were calculated from measurements of the displacement of a drop of naphthalene monobromide which was positioned in a capillary tube separating the volumes of gas on either side of the wire specimen. Table 7.2

TABLE 7.2

Apparent mobilities of absorbed hydrogen as protons[1]

Temperature °	μ_{H^+}(cm² volt⁻¹ sec⁻¹) Calculated from experimental measurements of transport numbers	Calculated from values of D obtained by Jost and Widmann (1935)—cf. Table 7.1
182	$1{\cdot}46 \times 10^{-4}$	$2{\cdot}7$–$3{\cdot}8 \times 10^{-4}$
240	$2{\cdot}80 \times 10^{-4}$	$4{\cdot}9$–$6{\cdot}9 \times 10^{-4}$

[1] Wagner and Heller (1940).

shows that the values of mobility μ_{H^+} calculated from these transport numbers were in reasonable agreement with values calculated from D_α through the Nernst–Einstein relationship $\mu_{H^+} \cdot kT = D_\alpha$.

K. General Considerations of the Diffusion of Hydrogen in Electrodes

Electrochemical considerations arise when either side of a diffusion membrane is in contact with solution. When electrolyte is present at both sides, the membrane can be termed a bielectrode. A number of experimental investigations have been made of the course of permeation of hydrogen through such bielectrodes when hydrogen has been discharged at one of its faces which is often termed the "polarization" side. A diagrammatic representation of a bielectrode in the form of a disc has been shown in Fig. 2.15 although, again, an alternative possibility is for it to be in tube form (Barton and Lewis, 1961; Cleary and Greene, 1965).

There were doubts in early investigations (Ferguson and Dubpernell, 1933) that the hydrogen was being transmitted through the bulk lattice and not through pores or faults in the membrane or through faulty junctions between the membrane and the walls of the containing vessel. Clear experimental evidence of lattice diffusion was, however, obtained by Frumkin and Aladzhalova (1944) from considerations of

electrode potential measurements at both sides of the electrode during electrolysis and with different electrolytes in the diffusion and polarization compartments.

The amount of hydrogen being discharged electrolytically at the polarization face of the bielectrode can be calculated from the current in the polarization compartment. In some experiments, however (Kovba and Bagotskaya, 1963) estimates also have been made, by means of a gas burette, of the volume of hydrogen which is concurrently evolved at the polarization face, and so enables an additional check on the efficiency of transfusion. Clearly this efficiency can be obtained by measuring the volume of hydrogen evolved in the diffusion compartment, and this also has been estimated by the use of gas burettes.

An alternative method has been to measure the extent of reduction of a standardized solution of an oxidizing agent contained in the diffusion compartment (Schuldiner and Hoare, 1956). However, there are problems in this method due to unquantitative reduction and concurrent evolution of hydrogen as bubbles (La Pietra and Castellan, 1964). Latterly, permeation rates also have been estimated from measurements of the current in a potentiostatic circuit in which the diffusion side of the electrode is held at a positive potential corresponding to a negligibly low value of H/Pd (Devanathan and Stachurski 1962; von Stackelberg and Ludwig, 1964).

As a general technique, cathodization of the polarization side of a bielectrode provides an often useful means of altering the hydrogen content of the diffusion side of the electrode and/or of introducing hydrogen into the diffusion compartment without resort to electrolysis in this compartment itself. Recently, there have perhaps been a larger number of related studies in which only one side of the membrane is in contact with electrolyte and the other is in contact with gaseous hydrogen. In experiments of this general type, permeation rates can be calculated from measurements of changes in the volume of hydrogen at the gas phase side. When the side of the membrane in contact with electrolyte is cathodically polarized, there will be an overall production of hydrogen gas. Measurements of the rate of permeation of this gas through the membrane in such experiments have been obtained as a function of current density membrane thickness and temperatures have been obtained by Barrer (1940), Heath (1952) and Wahlin and Naumann (1953). Recently (using Pd/Ag alloys rather than pure palladium), this general technique has been adopted as a workable method of generating quantities of ultra pure hydrogen without the necessity of handling and storing cylinders (Darling, 1963; Jacobsen, 1965). In general, however, rather more attention has been paid to the reverse

situation where hydrogen gas diffuses continually through the membrane and is oxidized at the interface with the electrolyte. This interface can thus act as the anode of a fuel cell (Busson *et al.*, 1963; Lederer and Greene, 1963; von Sturm and Kohlmüller, 1965; Cleary and Greene, 1965); although whether at the moment this principle can be economically competitive seems still largely unresolved. This general set-up has also been suggested as useful for electrophoresis measurements (Neihof and Schuldiner, 1960).

L. Problems in the Determination of Diffusion Coefficients from Electrochemical Experiments

In principle, the rates of permeation of hydrogen measured during electrochemical experiments also can be made use of for calculation of diffusion coefficients. However, once again, in steady-state experiments application of the Fick first law diffusion equation requires that the concentration of hydrogen at the entrance and exit surfaces are accurately known. For surfaces in contact with electrolyte, the only reliable way by which this can be estimated at present is from measurements of electrode potential. At a face which is being cathodized, the component of potential which can be correlated with hydrogen content generally ought to be obtainable by extrapolations of open circuit measurements of E following interruption of electrolysis; but there is a general difficulty in ensuring that the surfaces have a sufficiently high catalytic activity for electrode potential measurements to be reliably correlated with hydrogen contents in terms of interconversion with p–C relationships.

Subsequent to studies by Frumkin and Aladzhalova (1944), measurements of electrode potential at both sides of a bielectrode as a function of the current density in the polarization compartment also have been made by Hoare and Schuldiner (1956, 1957b), Schuldiner and Hoare (1956, 1958); but the component of potential which can be related to hydrogen content was not separated from the total apparent potential at the polarization face, and measurements of permeation rates were not obtained.

So far the only "electrochemical" measurements of steady-state permeation rates which have been suitable for calculations of diffusion coefficients have been made with only one face in contact with the electrolyte; and these have only been obtained for β-phase concentrations of the Pd/H system and for a Pd/Ag alloy as described in a following section.

An alternative method of calculating D_α by means of measurements

with a bielectrode has been employed by using a variant of Barrer's (1940) break through techniques in which the potential of both sides of the bielectrode were potentiostatically controlled and D_α calculated from current-time curves of the circuit at the diffusion side following cathodization of the polarization side at a very low current density. Values of $D\alpha$ at ambient room temperature of $1{\cdot}3 \pm 0{\cdot}2 \times 10^{-7}$ and of $1{\cdot}6 \pm 0{\cdot}5 \times 10^{-7}$ have been obtained by Devanathan and Stachurski (1962) and by von Stackelberg and Ludwig (1964), respectively. These compare well with the value of $1{\cdot}6 \times 10^{-7}$ calculated from steady-state (gas phase to gas phase) permeation rates by Jewett and Makrides (1965). Simons and Flanagan (1965a), using the more recent p–C relationships of Wicke and Nernst (1964), have suggested that these rates may need to be corrected to $\sim 3{\cdot}0 \times 10^{-7}$.

Simons and Flanagan (1965a) have themselves measured D_α at temperatures between 0 and 50° by a further technique in which the rate of overall absorption of hydrogen into the bulk of their wire

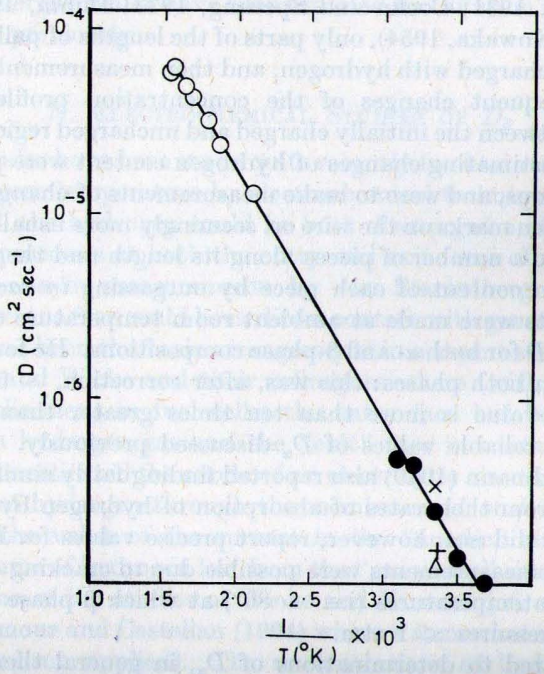


Fig. 7.5 Arrhenius plot of values of D_α (after Simons and Flanagan, 1965a). ○, Davis (1955); Katz and Gulbransen (1960); ×, adjusted result of Jewett and Makrides (1965); +, von Stackelberg and Ludwig (1964); △, Devanathan and Stachurski (1962); ●, Simons and Flanagan (1965a).

specimens has been calculated from measurements of electrical resistance whilst the changing surface concentration was obtained from measurements of electrode potential. These authors obtained a value of $2{\cdot}5 \times 10^{-7}$ for D_α at 25°.

A graph after Simons and Flanagan of D_α against $\frac{1}{T}$ in which they compare their results with those of other workers is shown in Fig. 7.5. In terms of the equation $D = D_0 e^{-E/RT}$, their line of best fit corresponds to $6{\cdot}1 \times 10^{-3} e^{-5990/RT}$ which compares with the following relationships suggested earlier: $1{\cdot}5 \times 10^{-2} e^{-6880/RT}$ (Barrer, 1940); $5{\cdot}95$–$8{\cdot}43 \times 10^{-3} e^{-5720/RT}$ (Jost and Widmann, 1935, 1940); $5{\cdot}18 \times 10^{-3} e^{-5650/RT}$ (Toda, 1958) and $4{\cdot}3 \times 10^{-3} e^{-5650/RT}$ (Katz and Gulbransen, 1960).

M. Diffusion of Hydrogen in the β-phase

In some measurements in the 1930s (Coehn and Specht, 1930; Coehn and Jürgens, 1931; Coehn and Sperling, 1933; Duhm, 1935; cf. also Sugeno and Kowaka, 1954), only parts of the lengths of palladium wires or foils were charged with hydrogen, and then measurements were made of the subsequent changes of the concentration profile across the boundary between the initially charged and uncharged regions. Duhm's methods of estimating changes of hydrogen content were probably the least ambiguous, and were to make measurements of changes in the distances between marks on the wire or, seemingly more usually, to cut the specimen into a number of pieces along its length and then to measure the hydrogen content of each piece by outgassing *in vacuo*. Duhm's measurements were made at ambient room temperature and he made estimates of D for both α- and β-phase compositions. He found the same value of D in both phases: this was, after correction, $\sim 5 \times 10^{-6}$ cm^2 sec^{-1}. This value is more than ten times greater than the highest of the more reliable values of D_α discussed previously. Nonetheless, Jost and Widmann (1940) also reported finding fairly similar values for D_α and D_β from their rates of absorption of hydrogen by a palladium sphere: they did not, however, report precise values for D_β, for which only limited measurements were possible due to cracking of the sphere at the lower temperatures (i.e. $\sim 80°$) at which β-phase hydrides are formed at pressures $\leqslant 1$ atm.

As compared to determinations of D_α, in general there are rather greater experimental inconveniences in obtaining D_β from more direct measurements of rates of permeation through a membrane for which H/Pd corresponds to β-phase compositions at both entrance and exit

surfaces. For instance, not only are there the increased design problems of coping with stresses due to dimensional changes of the membrane, but also, at temperatures $> ca\ 160°$ corresponding gas pressures at both faces must exceed one atmosphere because of the form of the p–C relationships. At lower temperatures, there are once again the problems of obtaining sufficiently highly catalytic surfaces for the overall permeation rate to be controlled by diffusion through the solid but recently, in tackling this general problem at 25° Jewett and Makrides (1965) have obtained measurements of D_β as well as D_α. They found D_β to have a value of $\sim 1{\cdot}5 \times 10^{-6}$ cm^2 sec^{-1} which was ~ 10 times higher than their value for D_α ($1{\cdot}6 \times 10^{-7}$). Recently, extrapolation of independent analogous measurements by Wicke and Bohmholdt (1964) supports this estimate in yielding $D_\beta = 1{\cdot}4 \times 10^{-6}$ at 25° with surfaces activated by plating on layers of palladium black. Wicke and Bohmholdt have obtained values of D_β at other temperatures within the range 30–100° from which they have calculated an activation energy of -5700 ± 200 cal which is within the range of values of activation energies which have been reported for diffusion in the α-phase as discussed previously.

N. Electrochemical Studies of D_β

Attempts also have been made quite recently to obtain measurements of D_β near room temperature by electrochemical techniques. Again, in such studies, the hydrogen could be both discharged and removed by electrolytic processes at both the entry and exit faces of a bielectrode, respectively—as in measurements by von Stackelberg and Ludwig (1964); or else one face could be in direct contact with gaseous hydrogen. This latter has been the basic arrangements in a recent series of studies by Küssner and Wicke and their colleagues where (with relevance to possible applications in fuel cells) the entry face has been in direct contact with hydrogen gas and the "exit" face in contact with electrolyte, and constituted the anode of an electrolytic circuit. The rate of permeation of hydrogen through the membrane (J or ϕ) was equated either with the value of the current in the "anodic" circuit, or else with the volume of hydrogen lost from the "gas phase" side of the membrane in some of the studies of Wicke and Küssner [cf. also measurements of Damour and Castellan (1964) where a somewhat more indirect analysis has been applied]. The concentrations of hydrogen, C, at surfaces in contact with electrolyte again can be derived from relationships between hydrogen content and electrode potential, but the corresponding component of overpotential during electrolysis has to be

estimated by extrapolation of plots against time of open-circuit measurements of electrode potential made after interruption of electrolysis and by using a Luggin capillary connection to the reference electrode (Wicke and Holleck, 1965).

Von Stackelberg and Ludwig have estimated D_β by measuring the rate of disappearance of the concentration (potential) gradient across the specimen after the switching off of electrolysis—and have obtained quite a high value of $\sim 5 \times 10^{-6}$ which compares with that reported by Duhm (*loc. cit.*). A similar principle has recently been used to obtain measurements of diffusion coefficients in a 25% Ag–75% Pd alloy by Wicke and Holleck (1965).

Alternatively, D_β can again be calculated from a knowledge of the concentration gradient across the membrane together with a measurement of the rate of permeation of hydrogen after a steady-state has been established. Values for the permeation rate have been equated with the current flow in the anodic circuit of which the exit face constitutes the anode (Küssner and Wicke, 1960). Using this latter technique, Wicke and Holleck (1965) have recently reported obtaining values ($\sim 7{\cdot}5 \times 10^{-7}$ cm^2 sec^{-1} at 25°) for D for a 25% Ag alloy which were in quite good agreement with a value ($6{\cdot}1 \times 10^{-7}$) obtained from straightforward measurements of permeation rates with gaseous hydrogen on both sides of the membrane (Wicke and Bohmholdt, 1964).

O. Presence of an α-/β-phase Boundary Within the Membrane under Steady-State Conditions

In earlier experiments of Wicke with Küssner (1960) and in the experiments of von Stackelberg and Ludwig (1964), the region of β-phase did not extend completely from the entry to the exit surface—since the latter was maintained at $C \approx 0$ by an appropriate setting of a potentiostat. In these circumstances, the concentration gradient through the membrane can be represented diagrammatically as shown in Fig. 7.6.

Von Stackelberg and Ludwig (1964) believed from an analysis of their results that, at the higher range of current densities ($\sim$250 mA cm^{-2}) which they employed, the region of β-phase extended over about 99% of the distance across the membrane—and estimated D to be $3(\pm 1) \times 10^{-6}$. This compares well with a value of $2{\cdot}85 \times 10^{-6}$ also determined recently by Cleary and Greene (1965) in somewhat analogous experiments. The case where there is direct contact with hydrogen gas at both entry and exit surfaces has also been recently examined by Jewett and Makrides (1965). These authors made measurements of rate of permeation through a membrane with β-phase compositions at the surface

of entry, and where there was continuous evacuation at the exit surface so that here $C \approx 0$. Results were compared with a theoretical relationship derived by Ash and Barrer (1960) (cf. also Küssner and Wicke,

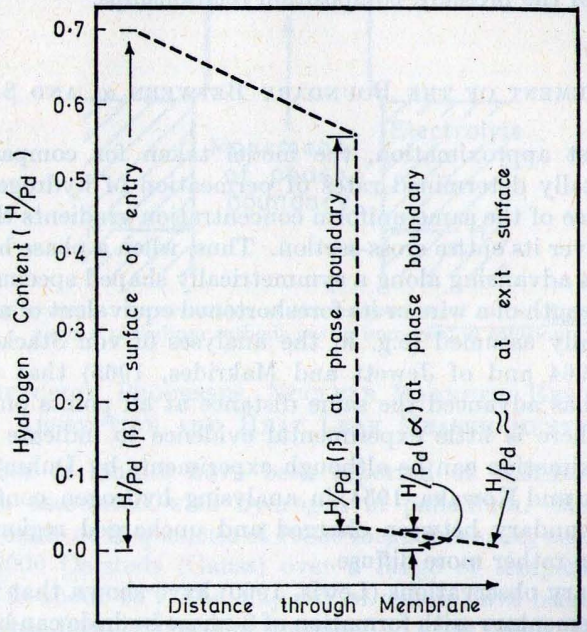


Fig. 7.6 Diagrammatic representation of the concentration gradient through a palladium membrane containing an α, β-phase boundary, during steady-state hydrogen permeation with a pressure of ~1 atm H_2 at the input surface, and very low concentrations of hydrogen at the exit surface at *ca* 25° (cf. von Stackelberg and Ludwig, 1964).

1960; Cleary and Greene, 1965) as appropriate to these conditions. This was:

$$J = \frac{D_\beta (C_0 - C_1) + D_\alpha C_2}{L} \tag{7.5}$$

where, in the convention of Jewett and Makrides, C_0 is the concentration (β-phase) at the entry surface, C_1 the β-phase concentration at the phase boundary, C_2 the α-phase concentration at the phase boundary and L the thickness of the membrane. They found good overall agreement between permeation rates obtained experimentally and those calculated from this theoretical relationship, which seemed to lend a general support both to the applicability of the relationship and to those measurements which indicate that D_β is 10–30 greater than D_α at around room temperatures. It may be noted that differences were found

by Jewett and Makrides between the plots of $p^{\frac{1}{2}}$ against permeation rate depending on whether the pressure was being increased or decreased—and these differences were suggested to be a reflection of hysteresis of the pressure–composition relationships.

P. Movement of the Boundary Between α- and β-phases

As a first approximation, the model taken for comparison with experimentally determined rates of permeation of hydrogen assumes the existence of the same uniform concentration gradients through the specimen over its entire cross-section. Thus, when a phase boundary is regarded as advancing along a symmetrically shaped specimen such as along the length of a wire or its foreshortened equivalent of a plate, it is also generally assumed (e.g. in the analyses of von Stackelberg and Ludwig, 1964 and of Jewett and Makrides, 1965) that the phase boundary has advanced the same distance at all points on the cross-section. There is little experimental evidence to indicate how valid this approximation can be although experiments by Duhm (1935) (cf. also Sugeno and Kowaka, 1954) in analysing hydrogen content across a phase boundary between charged and uncharged regions suggests this may be rather more diffuse.

Preliminary observations (Lewis, 1960) have shown that the expansion complementary with formation of β-phase hydride can be sufficient for changes in the dimensions of specimens around the boundary to be observed optically but no kinetic measurements have so far been obtained. Some semiquantitative measurements of the rate of permeation of β-phase regions have been made by taking a series of X-ray photographs, at intervals of time over a period of ~ 2 days, at short distances above an initial base line formed by the level of electrolyte (Fig. 7.7) whilst the wire below the electrolyte was subjected to a continuous electrolytic discharge of hydrogen (Smith and Barrett, 1940). Although there was no means of determining the exact concentration gradients, the measurements indicated that there was a gradual decrease with time in the average rate of advance of β-phase regions for which estimates ranged from 0·126 to 0·27 mm/hr.

In general, experiments have to be carefully designed in order to prevent hydrogen migrating forward from the initial datum line in other ways than through the solid lattice—particularly since expansion of the specimen can stress and crack films of many otherwise convenient materials (e.g., soft glass) which might be coated over the region into which the hydrogen is diffusing.

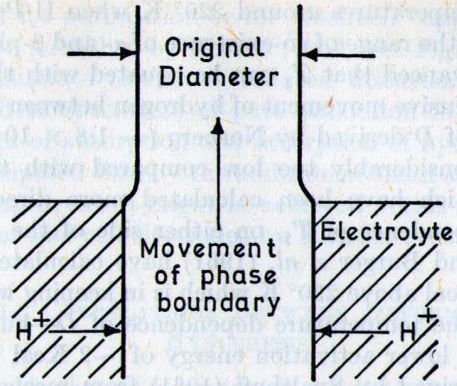


Fig. 7.7 Diagrammatic representation of the movement of an α, β-phase boundary along a palladium cathode partly immersed in solution.

Q. Diffusion Processes, Nuclear Magnetic Resonance Absorption and Heat Leak Measurements

A number of studies have been reported of N.M.R. absorption phenomena associated with hydrogen in palladium. Measurements have been made at frequencies of 10–30 megacycles/sec, using magnetic fields of 7000 Oersteds (Gauss) over a range of temperatures from −190° up to about 40°. The majority of results have been made with samples in the form of powders contained in glass phials, although the measurements of Norberg (1952) were made with wires, for which hydrogen contents were estimated both from measurements of electrical resistance, and from estimates of resonance shifts which could be related with changes of magnetic susceptibility.

Measurements have been made of the line widths of the resonance absorption, and also of the spin-lattice relaxation time T_1, and the spin-phase memory time, T_2. The results are similar in general type to what has been observed for the hydrides of other transition metals especially tantalum (Torrey, 1958; Spalthoff, 1961; cf. also Stalinski and Zogal, 1965). Minima in plots of the spin-lattice relaxation time, T_1, against temperature have been observed in the vicinity of 230–260° K by Norberg (1952), Torrey (1958) and Burger, Poulis and Hass (1961). Burger *et al.* (whose work included some studies with an alloy containing 2·8% iron) showed that the position of the minimum, and of the slopes of the relationships on either side of it, were dependent on the hydrogen content of the specimen. They also found that changes of hydrogen content produced even more pronounced effects on the form of the relationship between T_2 and temperature: this exhibited a

maximum at temperatures around 220° K when H/Pd was decreased to values within the range of co-existence of α- and β-phase hydrides.

It may be advanced that T_1 can be equated with the jump time τ, taken for the diffusive movement of hydrogen between interstitial sites, but the values of D derived by Norberg ($\sim 1{\cdot}8 \times 10^{-8}$ at room temperature) are considerably too low compared with the more recent values of D which have been calculated more directly. From the temperature dependence of T_1, on either side of the minimum, both Torrey (1958) and Burger *et al.* (1961) have calculated an activation energy of ~ 6 Kcal above 230° K which is in keeping with other values obtained from the temperature dependence of D—but below 230° K have obtained a lower activation energy of ~2 Kcal which compares with a value derived by Spalthoff (1961) from measurements of line widths.

Evidence of a diffusive process with a lower activation energy below 200° K has also been obtained from the temperature dependence of the rate of a slow release of heat ("heat leak") from specimens which had been rapidly cooled to lower temperature (Fritz *et al.*, 1961; Mitacek and Aston, 1963).

R. Diffusion of Hydrogen through Alloys of Palladium, and Improved Resistance to Deformation

The serious deformation of palladium specimens which can result from repeated cycles of absorption and desorption of hydrogen has been discussed in Chapter 3. Analogous cycles of gain and loss of hydrogen, with accompanying deformation, also can occur when specimens are repeatedly heated and cooled in an atmosphere of hydrogen at pressures exceeding that of the α- → β-phase transformation at the lower temperature of such a cycle. Such deformations have somewhat held back the use of palladium membranes for the purification of hydrogen on a commercial scale—since, although the problem can be reduced by maintaining the membrane at the higher temperature, this can be an inconvenience.

As yet a further observation in his early studies, Thomas Graham (1896b) had noted the virtual absence of irreversible changes of the dimensions of specimens of certain alloys with silver, nickel and platinum. Within the last decade (largely initiated by further studies reported by Hunter in 1957) alloys of palladium with silver contents ranging from 20 to 26% now seem in many instances to have superseded pure palladium for use as permeation membranes in the transmission of hydrogen discharged by electrolysis or else obtained from the

gas phase either for purification or for "fuel cell" applications. Photographs have been published by Hunter (1960) (see Fig. 3.4) and Darling (1963) which illustrate the much reduced distortion of such Pd/Ag alloys compared to specimens of pure palladium following a similar number of cycles of absorption and desorption of hydrogen. It might perhaps be anticipated that by the addition of small amounts of boron, a still further improvement might be achieved in this respect similar to that obtained for fuel cell electrodes by Küssner (1965).

S. Possible Correlations Between Deformation and Hysteresis

It seems probable that an important factor in the larger deformations observed with palladium specimens is the imperfectly reversible dimensional changes associated with migration of phase boundaries during α- → β- and β- → α-phase transformations. It has been proposed (Carson *et al.*, 1959, 1960) that there should be an increased resistance to deformation by alloys of palladium for which the form of the p–C relationships at the lower temperature of the cycle (generally room temperature, in practice) would be supercritical so that phase transformations would not occur during absorption and desorption no matter what range of pressures is employed. For a number of alloy systems, the magnitude of the critical temperature, T_c, with reference to the co-existence of two phases, decreases with increasing concentration of the alloying element as discussed in Chapter 6.

For instance, evidence suggests that for alloys containing $\geqslant 15\%$ of Pt (or somewhat higher contents of Ni or Rh), corresponding p–C relationships would be of a supercritical type at 25°. Moreover, alloys with contents of Pt, etc., which just exceeded these limiting concentrations would still exhibit substantial solubility of hydrogen over workably convenient ranges of pressure so that reasonably high concentration gradients—and so rates of permeation—could still be obtained for practical purposes as discussed later. With regard to the Pd/Ag series of alloys, measurements within the temperature 0–*ca* 500°, [Sieverts and Hagen (1935) and Carson, to be published] have indicated that with increasing content of silver there is an overall decrease in the extent of hysteresis both of p–C relationships and of relationships between hydrogen content and electrical resistance.

Despite this, Fig. 7.8 shows that a form of hysteresis has still been found to appear in plots of permeation rate as a function of increasing and decreasing temperature during studies with a 26% Ag alloy, which has been found quite a satisfactory composition on general grounds of

resistance to deformation, even although the appearance of some minor surface distortions has been observed (Darling, 1964b).

As well as having an increased resistance to deformation, alloys containing 23–26% Ag have a further practical advantage in that membranes of the same thickness have been found to exhibit increased permeation rates compared to pure palladium with the same pressure

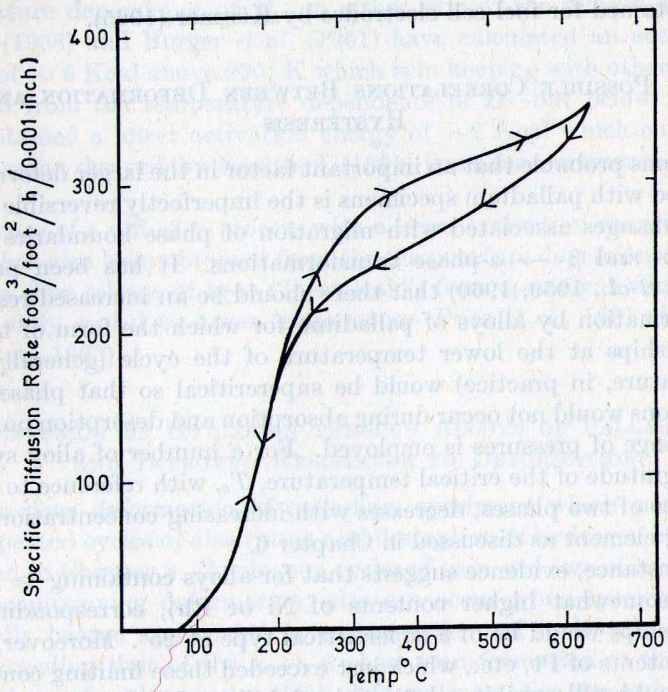


FIG. 7.8 Hysteresis of permeability exhibited by a 23% silver/palladium alloy—after Darling (1964b).

differentials at convenient temperatures. In addition to the use of Pd/Ag alloys, certain Pd/Pt and Pd/Au alloys have been proposed as further alternatives to the use of pure palladium and preliminary investigations have been reported with Pd/Boron alloys. It may be in the future that some of these or still other alloys may combine a high permeability together with a still further improved resistance to deformation (ideally combined with suitable mechanical properties which will allow of the use of very thin membranes) and finally a superior resistance to the corrosive attack of certain chemicals such as sulphur or mercury which can be troublesome to the Pd/Ag series.

T. Diffusion Coefficients for Hydrogen in Pd Alloys

As already mentioned previously, consideration of the Fick first law equation indicates that increased rates of permeation through certain Pd/Ag alloys, could be the result of higher concentration gradients across the membranes rather than to an increase of D.

Certainly trends in the p–C–T relationships for the Pd/Ag/H system (Sieverts *et al.*, 1915; Brodowsky and Poeschel, 1965) indicate it is probable that the solubility of hydrogen in alloys containing $\sim 30\%$ Ag can exceed the solubility in pure palladium over substantial ranges of pressure within the range of temperature of, for example, Darling's studies of permeation rates (cf. Fig. 7.8). Moreover, the relatively recent derivation by Brodowsky and Poeschel of fairly detailed p–C relationships for certain Pd/Ag alloys at quite low temperatures has made it possible for Wicke and Bohmholdt (1964) and Wicke and Holleck (1965) to derive values of D for a 25% Ag alloy from studies of permeation rates over the temperature range 30–100°. It has been found that D ($\sim 7 \times 10^{-6}$ at 25°) is about half the value of D in the β-phase hydride of pure palladium, although the diffusion process has virtually the same activation energy (~ 5700 cal mole^{-1}).

Quite recently, Piper (1966) has carried out some measurements of diffusion coefficients in Pd/Cu alloys and has reported a substantial increase in the value of D at 25° to $\sim 5 \times 10^{-5}$ for alloys containing $\sim 50\%$ Cu which have assumed a b.c.c. lattice structure.

CHAPTER 8

Absorption of Deuterium by Palladium and Alloys of Palladium: Separation of Hydrogen Isotopes

A. Comparison of p–C–T Relationships for the Pd/H and Pd/D Systems

The first measurements of the solubility of deuterium in palladium were obtained in 1935 by Sieverts and Zapf who recorded solubilities

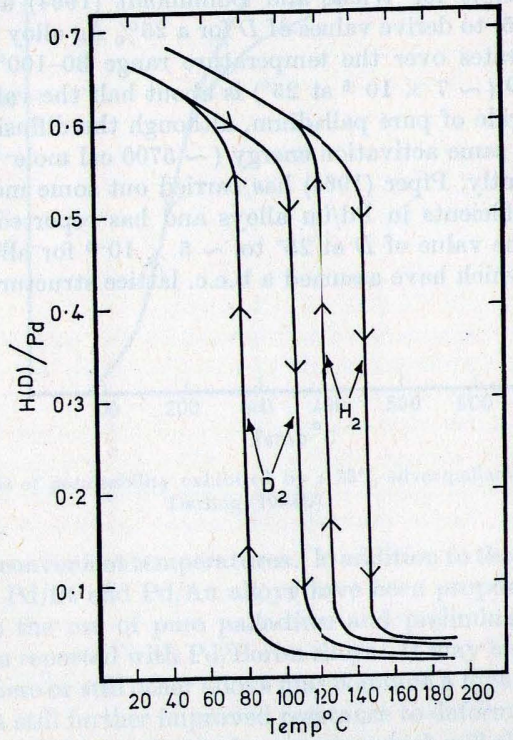


Fig. 8.1 Comparison of solubilities of hydrogen and deuterium in palladium at temperatures up to 200° under gaseous pressures of 740 mm Hg, showing "hysteresis" between sequences of measurements made during stepwise increases and decreases of temperature, respectively—after Sieverts and Danz (1937).

under a pressure of 740 mm Hg at a series of temperatures up to 1100°. These measurements were largely confirmed in a more comprehensive series of experiments by Sieverts with Danz (1937) and a plot of isobaric solubilities under 740 mm Hg is shown in Figs 8.1 and 8.2 extending over a range from 25 to 400°.

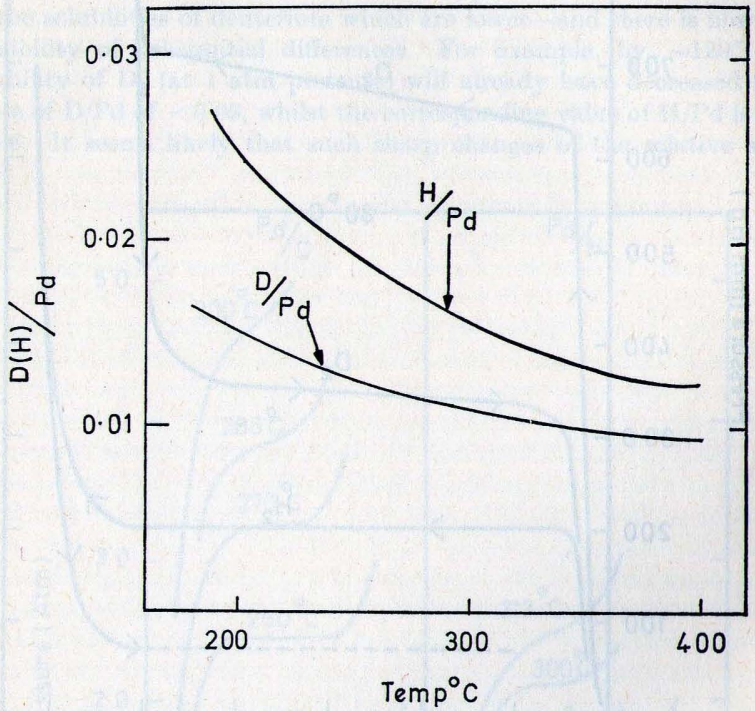


Fig. 8.2 Comparison of the solubilities of H_2 and D_2 in palladium under 740 mm Hg at temperatures >180°—after Sieverts and Danz (1937).

These figures indicate that the solubility of deuterium, as compared at about 1 atm pressure, is everywhere lower than that of hydrogen (protium) although the relative magnitude of the difference seems to decrease somewhat with increasing temperature. This lower solubility of deuterium at any given pressure is also indicated by a comparison of complete isotherms which were obtained by Sieverts and Danz at 80, 100 and 120°. The plot of the 80° isotherms is shown in Fig. 8.3 and not only illustrates the lower deuterium solubility but also indicates that the Pd/D isotherms exhibit an analogous hysteresis to the Pd/H isotherms over this range of temperatures. It also shows that the

vapour pressure of deuterium over regions of α- and β-phase deuteride co-existence substantially *exceeds* the corresponding pressure of hydrogen.

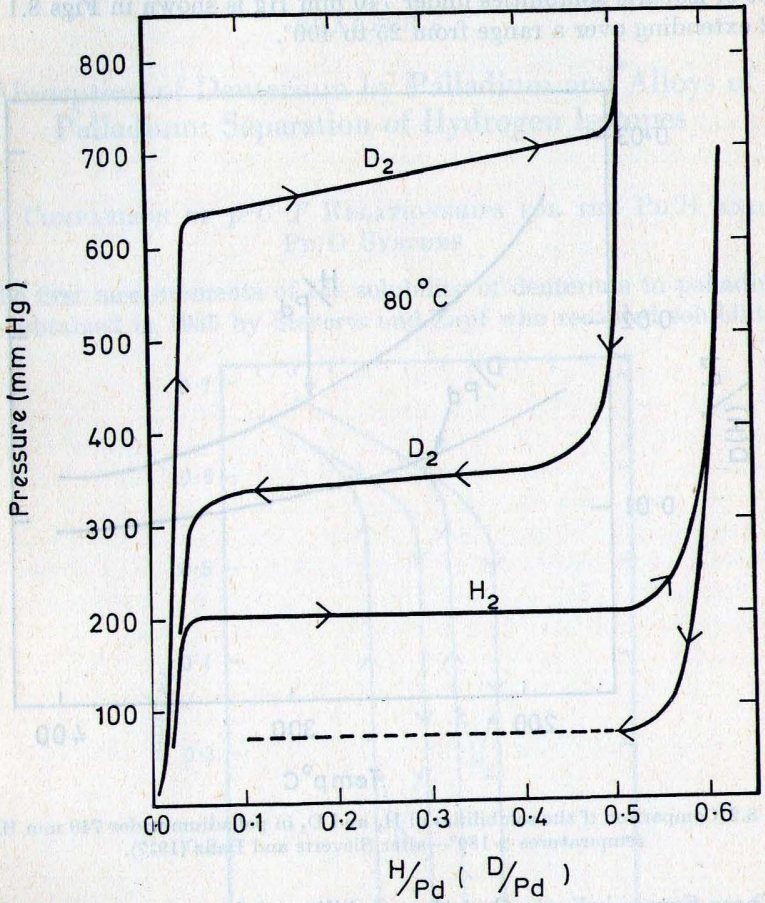


FIG. 8.3 Comparison of p–C relationships for the Pd/H and Pd/D systems at 80°—after Sieverts and Danz (1937).

The discontinuities in the isobaric plots in Fig. 8.2 correspond with the temperatures over which the α- → β-phase and β → α-phase transformations occur. At temperatures lower than at a particular discontinuity, the equilibrium content of the solid will correspond to a fully transformed β-phase hydride or deuteride. On the other hand, at higher temperatures (i.e. in this particular case at temperatures above that at which the pressure over regions of α- and β-phase co-existence

attains 740 mm Hg) the content of the solid would correspond to only α-phase compositions. Clearly, differences in the relative solubilities of hydrogen and deuterium can be especially large at temperatures adjacent to these discontinuities. For the Pd/D system, the pressure over the region of two phase co-existence exceeds 1 atm at a lower temperature than is the case for the Pd/H system. Thus it continues to be the solubilities of deuterium which are lower—and there is now the possibility of substantial differences. For example, by ~120°, the solubility of D_2 (at 1 atm pressure) will already have decreased to a value of D/Pd of <0·05, whilst the corresponding value of H/Pd is still ~0·6. It seems likely that such sharp changes of the relative solu-

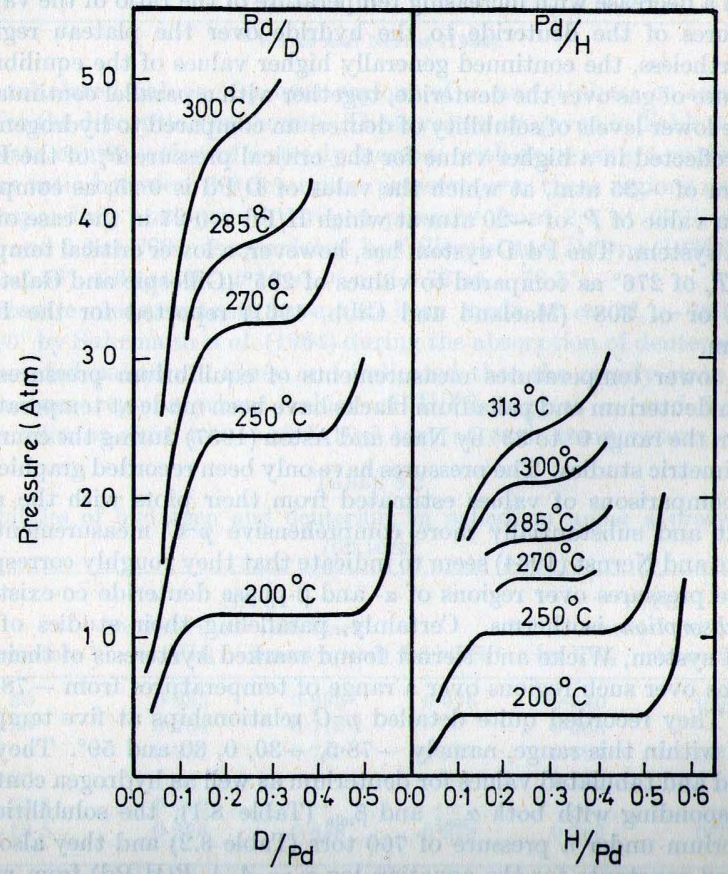


FIG. 8.4 Comparison of p–C "*absorption*" isotherms near T_c for Pd/D—after Gillespie and Downs (1939), and Pd/H—after Gillespie and Galstaun (1936).

bilities of the isotopes over certain narrow ranges of pressure and/or temperature could be a main factor governing the dependence of the separation factor for hydrogen and deuterium between the solid and gaseous phases as a function of the pressure of gaseous mixtures which has been briefly reported by Andreev and Tsionskii (1964).

Subsequent to Sieverts and Danz's studies, measurements of equilibria between palladium black and deuterium gas were obtained by Gillespie and Downs (1939) (see Fig. 8.4) over the temperature range 200–300° at a range of pressures extending up to ~50 atm. These authors also found evidence of hysteresis in the relationships at temperatures up to 270°. Comparing their measurements with those of earlier analogous experiments with hydrogen, Gillespie and Downs noted a decrease with increasing temperature of the ratio of the vapour pressures of the deuteride to the hydride over the plateau regions. Nevertheless, the continued generally higher values of the equilibrium pressure of gas over the deuteride, together with a parallel continuation of the lower levels of solubility of deuterium compared to hydrogen, are also reflected in a higher value for the critical pressure P_c of the Pd/D system of ~35 atm, at which the value of D/Pd is 0·25, as compared with a value of P_c of ~20 atm at which H/Pd ~0·27 in the case of the Pd/H system. The Pd/D system has, however, a lower critical temperature T_c of 276° as compared to values of 295° (Gillespie and Galstaun, 1936) or of 308° (Maeland and Gibb, 1961) reported for the Pd/H system.

At lower temperatures measurements of equilibrium pressures between deuterium and palladium blacks have been made at temperatures within the range 0° to 33° by Nace and Aston (1957) during the course of calorimetric studies. The pressures have only been recorded graphically, but comparisons of values estimated from their plots with the more recent and substantially more comprehensive p–C measurements of Wicke and Nernst (1964) seem to indicate that they roughly correspond to the pressures over regions of α- and β-phase deuteride co-existence for *absorption* isotherms. Certainly, paralleling their studies of the Pd/H system, Wicke and Nernst found marked hysteresis of their isotherms over such regions over a range of temperatures from −78·5 to 50°. They recorded quite detailed p–C relationships at five temperatures within this range, namely −78·5, −30, 0, 30 and 50°. They obtained and tabulated values for deuterium as well as hydrogen contents corresponding with both α_{max} and β_{min} (Table 8.1), the solubilities of deuterium under a pressure of 760 torr (Table 8.2) and they also calculated constants for the equation $\log p = A + B(\text{H/Pd})$ from which relationships in the β-phase can be derived at higher pressures. They

TABLE 8.1

Some values of H/Pd and D/Pd, respectively, at $\alpha_{(max)}$ and $\beta_{(min)}$[1]

Temperature°	H/Pd $\alpha_{(max)}$ (±0·0005)	H/Pd $\beta_{(min)}$ (±0·003)	D/Pd $\alpha_{(max)}$ (±0·0005)	D/Pd $\beta_{(min)}$ (±0·003)
75	0·0160	—	0·0190	—
60	0·0135	—	0·0155	—
50	0·0120	0·599	0·0150	0·587
30	0·0090	0·608	0·0103	0·600
0	0·0055	0·615	0·0065	0·609
−30	—	0·629	—	0·616
−78·5	—	0·635	—	0·625

[1] Wicke and Nernst (1964).

also tabulated values of p over regions of α- and β-phase co-existence $p_{\beta,\alpha}$ for the desorption isotherms. These values are given in Table 8.3 and indicate continuation of a steady increase with decreasing temperature in the ratio between the deuterium pressure over these regions and the corresponding analogous hydrogen pressure from 2·1 at 270°, 2·4 at 250° and 2·9 at 200°, as calculated by Gillespie and Downs (1939) up to 4·32 at 50°, 4·64 at 30°, 5·13 at 0° and 6·73 at −78·5°.

Pressure measurements have also been made at *ca* 22, −78·5 and −196° by Suhrmann *et al.* (1964) during the absorption of deuterium by evaporated palladium films, and indicated that the steady-state pressures over regions where values of D/Pd suggest α- and β-phase deuterides co-exist are ~10^{-2}–10^{-3} torr at each temperature, which

TABLE 8.2

Solubilities of hydrogen and deuterium in palladium under a pressure of 760 torr[1]

Temperature °	H/Pd Pd activated by UH_3	H/Pd Pd black (unactivated)	H/Pd Pd black[2]	D/Pd Pd activated by UD_3	D/Pd Pd black (unactivated)
50	0·683	0·695	0·676	0·640	0·639
30	0·704	0·715	—	0·666	—
0	0·737	0·749	0·717	0·697	0·684
−30	—	—	—	0·730	—
−33·8	0·772	—	—	—	—
−78·5	0·826	0·838	0·870	0·783	0·776

[1] Wicke and Nernst (1964).
[2] Perminov *et al.* (1957).

TABLE 8.3

Some values of pressures ($p_{\beta,\alpha}$) over regions of α- and β-phase co-existence during desorption of hydrogen and deuterium, respectively[1]

Temperature °	$p_{\beta,\alpha}$ (torr) Pd/H	Pd/D
50	23·0 ± 0·7	99·4 ± 1·5
30	8·4 ± 0·3	39·0 ± 0·8
0	1·52 ± 0·05	7·8 ± 0·1
−30	—	1·05 ± 0·02
−33·8	0·133 ± 0·003	—
−78·5	0·00156 ± 0·0001	0·0106 ± 0·0005

[1] Wicke and Nernst (1964).

seems too low a value at 22° and perhaps too high at −195° in comparison with the trend in Wicke and Nernst's analogous values. Results seemed insufficiently detailed to make very accurate estimates of maximum solubilities but at −195° they indicated that a value of D/Pd of ~1·5 had been attained. Doubts concerning values obtained for the solubilities of hydrogen in analogous experiments have been expressed in Chapter 2.

B. p–C–T Relationships Derived from Electrode Potential Measurements

Flanagan (1961) has carried out measurements of electrode potential in 0·02N DCl in D_2O saturated with D_2 gas at a pressure of 1 atm as a function of deuterium content during the absorption of deuterium by a palladium electrode over a temperature range from 0 to 28° [and subsequently, an analogous series of measurements were obtained for a series of Pd/Pt alloys by Maeland and Flanagan (1964)]. Flanagan derived p–C relationships from these results in the same way as for analogous measurements of the Pd/H system as described in Chapter 2. In the case of specimens which has been activated by anodization, he found the value of E over regions of co-existence of α- and β-phase deuterides to have a value of ~31 mV at 25° w.r.t. a Pt/D_2 electrode in the same solution. With similar appropriate connection to those discussed for a Pd/H electrode, this value of E corresponds with a derived value for the deuteride pressure of ~65 mm Hg at 25°. Values of 79 mm Hg were also quoted by Flanagan as derived from electrode potential measurements with specimens that had been palladized

(thinly coated with palladium black by electrodeposition) and so for which the surface concentration of hydrogen may have slightly exceeded the true steady-state "absorption" value because of a restricted rate of diffusion along thin dendrites into the bulk. These values of deuteride pressure compare with a value of 65 mm Hg at 25° calculated by Flanagan by interpolation of plots of the pressure over regions of α- and β-phase co-existence recorded at adjacent temperatures by Nace and Aston (1957). They also seem in keeping with analogous estimates of $p_{\alpha,\beta}$ which may be made from the later measurements of Wicke and Nernst (1964). Moreover, the equilibrium solubility of deuterium under a pressure of 1 atm at 25°, which was measured by Flanagan (D/Pd = 0·65), is also in good accord with the solubilities determined directly in gas/solid equilibria by Wicke and Nernst as given in Table 8.2.

C. Partial Molar Heats and Entropies of Absorption and Desorption of Deuterium: Heat Capacity Measurements

Heats of absorption derived from plots of log p against $\frac{1}{T}$ for values of p over ranges of co-existence of α- and β-phases as recorded by Gillespie and Downs over the range of temperatures from 200 to 270° give a value of 7700 cal/mole H_2. Values of $\Delta\bar{H}$, calculated analogously from the temperature dependence of the value of electrode potential over potential plateau regions within the temperature range 0–48° by Flanagan (1961) and from pressures over the range 0–33° by Nace and Aston (1957), have given rather higher values of 8795 and 8379 cal/mole H_2, respectively. Nonetheless, both these later values are still lower than values obtained in analogous determinations of $\Delta\bar{H}$ for the absorption of *hydrogen* by palladium.

A lower heat of absorption of deuterium as compared to hydrogen was also obtained by calorimetric determinations by Nace and Aston (1957) over regions of α- and β-phase co-existence. The average value for absorption of deuterium being reported as 8379 cal/mole compared with 9605 cal/mole for hydrogen. Values of heats of desorption of deuterium again were higher than the heats of absorption but were lower than the heats of desorption of hydrogen.

In general, values of $\Delta\bar{S}$ derived either by combination of partial molar heats and free energies through the Gibbs–Helmholtz equation or directly from the temperature dependence of the free energy, give values for the absorption of deuterium (−24·7 cal mole^{-1} deg^{-1}) which are slightly higher than the complementary value for the absorption of

hydrogen ($-23{\cdot}4$ cal mole^{-1} deg^{-1}). In general, therefore, it could be advanced that the reason for the lower value of $\Delta\bar{G}$ for the absorption of deuterium is partly accountable by the entropy term in addition to the differences between the heat terms.

Heat capacity measurements have fairly recently been carried out by Nace and Aston (1957) in conjunction with analogous measurements of the heat capacity of hydrogen. The most comprehensive series of measurements was made with a sample which has a deuterium content corresponding to an atomic ratio D/Pd = 0·479—at which composition there is co-existence of α- and β- phase deuterides at 25°. The heat capacity measurements were made within the range of temperatures 15·4° K to 300° K, though there was a gap over the range 152° K–279° K.

As for the Pd/H system, a plot of results presented in terms of heat capacity per mole D_2 also exhibited a λ-type anomaly over the temperature range from 40 to 80° K. The forms of the respective anomalies are compared in Fig. 8.5.

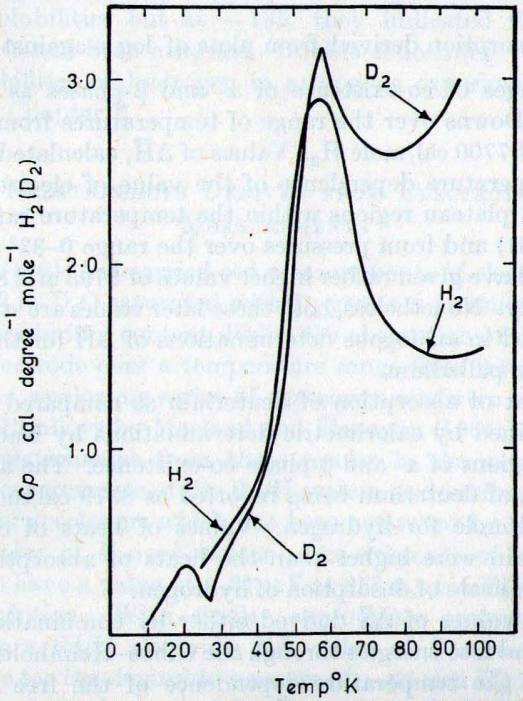


FIG. 8.5 Comparison of specific heat at low temperatures of hydrogen and deuterium absorbed in palladium black with H(D)/Pd ~ 0·5—after Nace and Aston (1957).

D. Variation of the Electrical Resistance of Palladium as a Function of Deuterium Content

Generally good agreement has been obtained between the results of the two studies (Sieverts and Danz, 1937; Flanagan, 1961) which have been made of the relationships between relative electrical resistance (R/R_0) and the deuterium content of palladium at *ca* 25°. The form of

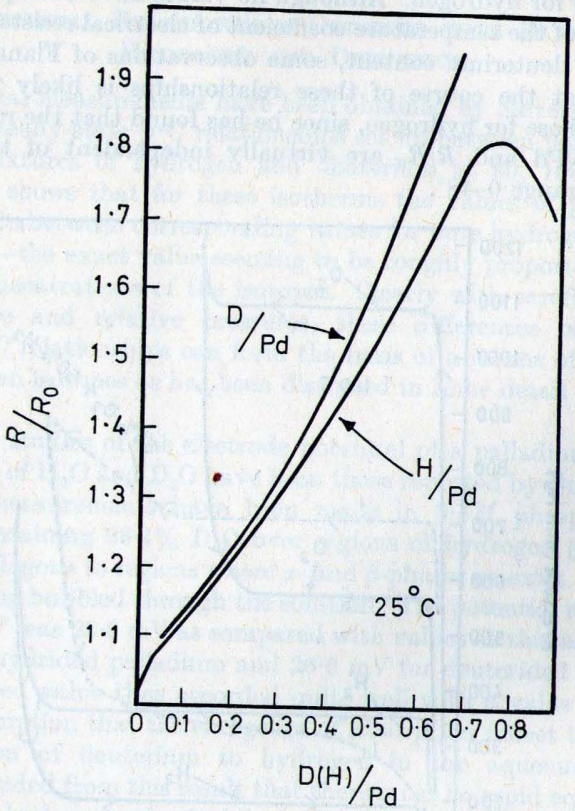


FIG. 8.6 Comparison of "absorption" relationships between R/R_0 and both D/Pd and H/Pd—after Flanagan (1961) and Barton *et al.* (1963a).

the relationships is compared with analogous relationships for hydrogen in Fig. 8.6. This shows that over the range of D/Pd where R/R_0 is increasing, the absorption of deuterium causes a greater increase of resistance atom for atom than does hydrogen, and the value of R/R_0 (~1·936) attains a higher maximum value than occurs in the curve for H/Pd (cf. also Suhrmann *et al.*, 1964). In general, however, the overall

form of the two relationships is very similar, and the evidence from concurrent measurements of electrode potential during absorption of deuterium is that the change of slope of the relationships when R/R_0 ~1·06 is again associated with the onset of the α- → β-phase transformation. The relationships which apply during the subsequent desorption of deuterium have not as yet been reported so that it is not possible to compare the relative degree of hysteresis with that of the corresponding relationship for hydrogen. Although no values have been published of the change of the temperature coefficient of electrical resistance, α, as a function of deuterium content, some observations of Flanagan (1961) indicate that the course of these relationships is likely to be very similar to those for hydrogen, since he has found that the relationships between D/Pd and R/R_0 are virtually independent of temperature within the range 0–48°.

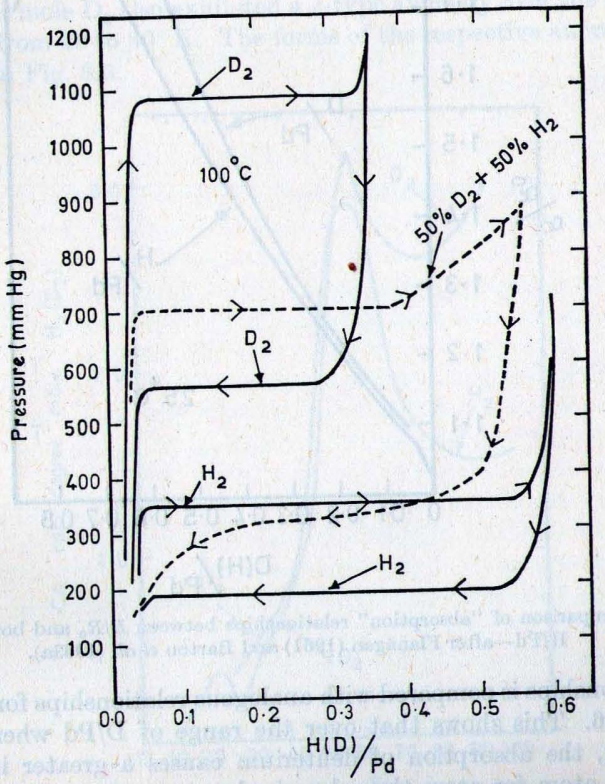


FIG. 8.7 Comparison of p–C relationships at 100° for equilibration between palladium and both pure H_2 and D_2, and a mixture of 50% H_2 + 50% D_2—after Sieverts and Danz (1937).

Relationships between R/R_0 and deuterium content have also been obtained by Maeland and Flanagan (1964) for a series of Pd/Pt alloys. Changes of the lattice structure and magnetic susceptibility of palladium as a function of deuterium content are discussed in the next chapter in conjunction with measurements of these parameters as a function of hydrogen content.

E. Isothermal Relationships Obtained with Mixtures of Hydrogen and Deuterium

Isothermal measurements have been obtained by Sieverts and Danz (1937) of steady-state p–C relationships set up between palladium and gaseous mixtures of hydrogen and deuterium at 80, 100 and 120°. Figure 8.7 shows that for these isotherms the values of pressure are intermediate between corresponding values for pure hydrogen and pure deuterium—the exact value seeming to be roughly proportional to the relative concentrations of the isotopes. Clearly with careful choice of temperature and relative pressures, these differences between the various p–C relationships can form the basis of a means of separating the hydrogen isotopes as has been discussed in some detail by Sieverts and Danz.

The only studies of the electrode potential of a palladium electrode in mixtures of H_2O and D_2O have been those reported by Bucur (1961), in which measurements have been made in 0·5M phosphoric acid solution containing 86·4% D_2O over regions of hydrogen (deuterium) content analogous to regions where α- and β-phases co-exist. Hydrogen gas was being bubbled through the solution. The potential recorded by Bucur at 30° was 28·9 mV as compared with values at this temperature of 46·5 for hydrided palladium and 26·6 mV for deuterided palladium. The measured value thus accorded quite well with a value calculated on the assumption that the energetics of absorption reflect the relative concentration of deuterium to hydrogen in the aqueous solution. Bucur concluded from this result that there must be rapid equilibration between the hydrogen adsorbed from the gas on to the palladized palladium electrode and the aqueous phase in accordance with the reaction

$$H_2 + 2D_2O \rightleftharpoons 2HDO + D_2$$

in order that the potential of the electrodes should indicate that they contained such a high content of deuterium in the presence of the bubbled stream of hydrogen dissolved in the solution.

F. Comparison of Diffusion Coefficients for Hydrogen and Deuterium

So far no attempts seem to have been made to calculate diffusion coefficients for deuterium in palladium from measurements of rates of permeation across a membrane when well established equilibria with gaseous deuterium have been set up at both input and exit sides at values of temperature and pressure for which the corresponding concentrations of dissolved deuterium can be derived.

On steric grounds (cf. values of lattice parameters in Chapter 9), the diffusion constant of the heavier isotope might be expected to be less than that of hydrogen, but, on the other hand, the lower heat of absorption might perhaps be expected to correspond with its having a slightly higher mobility.

A comparison of diffusion coefficients by Jost and Widmann (1935, 1940) has, in fact, suggested the deuterium has slightly the higher value of D. As also discussed in Chapter 7, the experimental method used by these authors was to measure the rates of the absorption of the isotopes by solid spheres suspended in each gas in turn: they found the ratio D_D/D_H to be $\sim 1{\cdot}3$ at *ca* 260°. It also was concluded by Schuldiner and Hoare (1958) that deuterium diffused through palladium faster than hydrogen under the same concentration gradient. Differences in the rates of diffusion of the isotopes through palladium tubes has recently been investigated as a means of separating hydrogen from tritium (Charalambus and Goebel, 1965).

G. Separation of Hydrogen Isotopes by Gas Chromatographic Techniques using Column Packings Coated with Palladium

Over the last ten years, a number of investigations have been made into the possibility of the separation of hydrogen isotopes by gas chromatographic techniques. One class of column packing which has been studied is that of palladium dispersed on materials such as asbestos or quartz. This general approach has been applied to the separation of hydrogen and tritium (Akhtar and Smith, 1964) as well as to the separation of hydrogen and deuterium although, so far, reports have only extended to attempts made at separations of batch samples in either case.

The general method of elution chromatography has been applied by Thomas and Smith (1959) using argon as a carrier gas. Complete separation of the whole of the sample was not reported as achieved, the most distinct separation being shown in Fig. 8.8. These authors found

the best temperatures for a sharp separation to be within the range 150–190°.

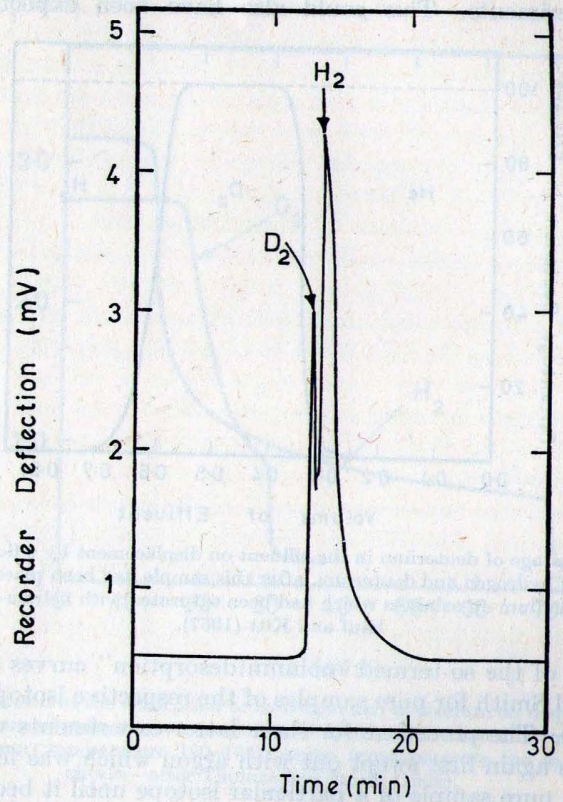


Fig. 8.8 Example of partial separation of deuterium and hydrogen by differential displacement by argon from a palladium packed column—after Thomas and Smith (1959) who give precise conditions.

Other information has been obtained by the "displacement" or "breakthrough" techniques. In these experiments, the column was again first saturated with an inert gas such as helium or argon before the sample was introduced. The sample was then followed on to the column either by pure hydrogen or else by a further flow of inert gas following the detection of the first fractions of the sample at the column outlet. Both Gluckhauf and Kitt (1957) and Thomas and Smith (1959) found that the first fractions of the sample contained virtually 100% D_2 as indicated by an example of results obtained by the displacement technique which are diagrammatically reproduced in Fig. 8.9.

An initial appearance of deuterium in front of hydrogen is in line with the fact that D_2 corresponds with the first peak detected in the elution experiments. This could also have been expected from a

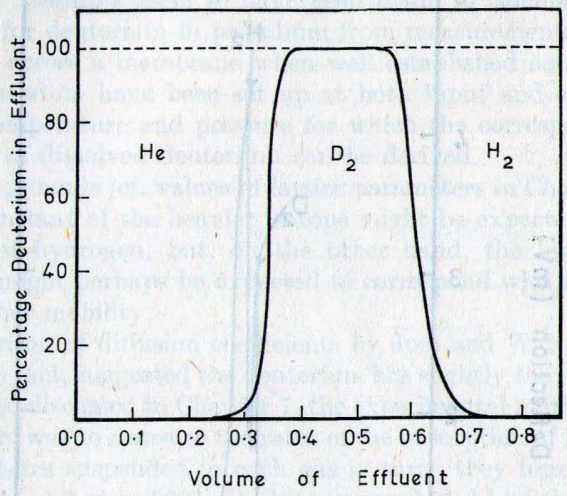


FIG. 8.9 Percentage of deuterium in the effluent on displacement by a flow of hydrogen of a mixture of hydrogen and deuterium, after this sample had been placed on a column containing palladium on asbestos which had been saturated with helium—after Glueckhauf and Kitt (1957).

comparison of the so-termed "column desorption" curves obtained by Thomas and Smith for pure samples of the respective isotopes as shown in Fig. 8.10. The procedure for these latter experiments was that the column was again first swept out with argon which was followed by a stream of a pure sample of a particular isotope until it became detectable at the outlet. At this point the flow of argon was resubstituted at the inlet. The curves in Fig. 8.10 represent the subsequent displacement of either hydrogen or deuterium from the column. Clearly, overall, hydrogen is shown to be retained longer on the column than deuterium. This could be accountable in terms of differences of diffusion coefficients of the two isotopes in palladium since their relative magnitudes (see above) indicate that deuterium would have the higher value. Another cause might be the generally higher solubility of hydrogen in the metal. However, it would also seem likely that a primary reason is the higher vapour pressure of deuterium compared to hydrogen, including in particular (see Fig. 8.3) those ranges of hydrogen (deuterium) content corresponding to regions of co-existence of α- and β-phases—which could perhaps have represented the composition of the dispersed layer over the "middle" regions of the "desorption"

curves in Fig. 8.10. A further paper reporting extensive additional work in this general field of study has recently been published by Botter *et al.* (1965).

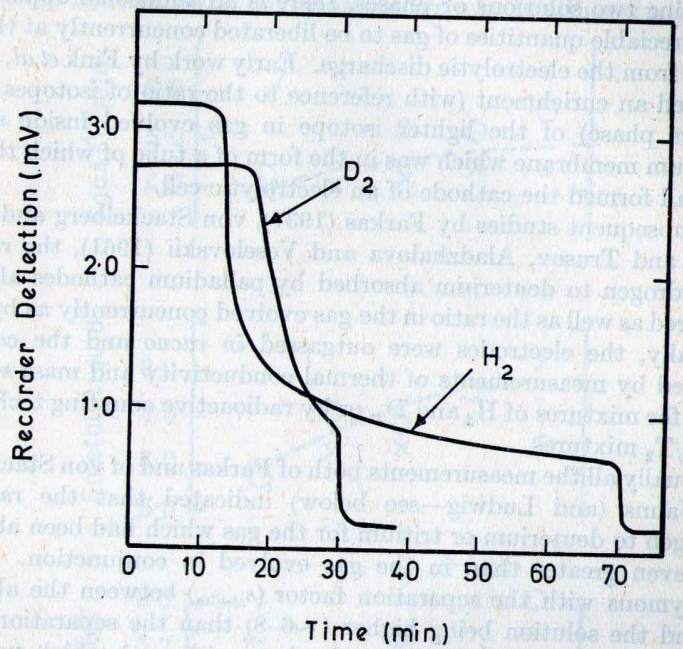


FIG. 8.10 Comparison of the desorption of hydrogen and deuterium on displacement by argon from columns of palladium on quartz which had been saturated in turn by hydrogen and deuterium: temperature 100–105°; argon input pressure the same for both curves—after Thomas and Smith (1959).

H. Factors Involved in the Separation of Hydrogen Isotopes During Electrolysis at Palladium Electrodes

During electrolysis of aqueous solutions, the ratio of hydrogen to deuterium in the gas evolved at the cathode is generally higher than the corresponding ratio of isotopes in the aqueous phase. This is complementary with an increasing relative concentration of deuterium in the electrolyte which has been the basis of one classical method of concentrating the heavier isotope. Using the symbol s to represent the "separation coefficient" this can be defined in this case as

$$s_{\text{gas/liq}} = (\text{H/D})_{\text{gas}}/(\text{H/D})_{\text{liq}}$$

where H/D represents the ratios of hydrogen to deuterium atoms in the evolved gas and in the solution, respectively.

When the cathode is formed of palladium or of a palladium alloy, there is a concurrent opportunity for the solid to absorb appreciable volumes of gas. When it is in the form of a membrane or bielectrode separating two solutions or phases, there is an additional opportunity for appreciable quantities of gas to be liberated concurrently at the side remote from the electrolytic discharge. Early work by Fink *et al*, (1934) indicated an enrichment (with reference to the ratio of isotopes in the aqueous phase) of the lighter isotope in gas evolved inside such a palladium membrane which was in the form of a tube of which the outside wall formed the cathode of an electrolytic cell.

In subsequent studies by Farkas (1937), von Stackelberg and Jahns (1958) and Trusov, Aladzhalova and Veselovskii (1961), the ratio of the hydrogen to deuterium absorbed by palladium cathodes also was measured as well as the ratio in the gas evolved concurrently as bubbles. Generally, the electrodes were outgassed *in vacuo* and the contents analysed by measurements of thermal conductivity and mass spectrometry for mixtures of H_2 and D_2, or by radioactive counting techniques for H_2/T_2 mixtures.

Virtually all the measurements both of Farkas and of von Stackelberg and Jahns (and Ludwig—see below) indicated that the ratios of hydrogen to deuterium or tritium for the gas which had been absorbed were even greater than in the gas evolved in conjunction. This is synonymous with the separation factor ($s_{abs/liq}$) between the absorbed gas and the solution being higher ($\sim$6–8) than the separation factor expressed with respect to the evolved gas ($s_{evolv/liq}$) which was only $\sim$4–5.

The finding by Ludwig of an even wider relative difference between the analogous separation factors for hydrogen and tritium was reported in the paper of von Stackelberg and Jahns—namely $s_{abs/liq}$ $\sim$10 and $s_{evolv/liq}$ $\sim$6, respectively. In general, these results might be regarded as in keeping with the higher vapour pressures of the Pd/D than the Pd/H isotherms as a function of hydrogen (deuterium) content, since this could be reflected by a higher overall rate of loss by desorption of the deuterium discharged by electrolysis. Nevertheless, quite opposite experimental results have been reported by Trusov *et al.* (1961). Although these latter authors obtained similar values ($\sim$8) for $s_{evolv/liq}$ (apart from one or two very high values) they also obtained values of $s_{abs/liq}$ which all were $<1\cdot4$.

Farkas (1937) obtained similar values for separation factors in both acidic and caustic solutions over a range of current densities up to $\sim$40 mA cm^{-2} although, as indicated in Fig. 8.11, von Stackelberg and Jahns believed that their results showed a dependence on current

density. Results in Fig. 8.11 also suggest the separation factors to be broadly independent of the activity of the surfaces, which is again in general agreement with Farkas' findings, although the "states" of activity are not defined in any quantitative way in either study.

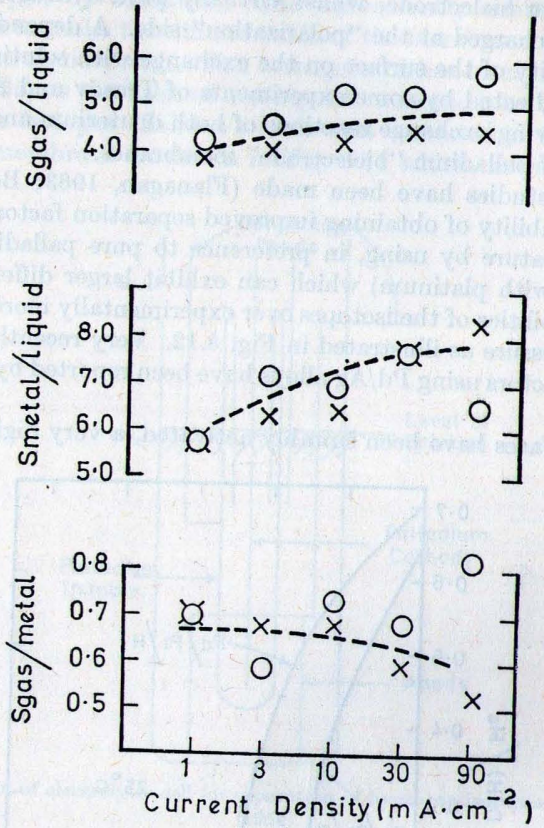


FIG. 8.11 Separation factors during electrolysis at palladium cathodes of different surface activities (○ and ×) as a function of current density—after von Stackelberg and Jahns (1958).

It also was assumed by both Farkas and by von Stackelberg and Jahns that there was a rapid equilibration of the chemisorbed hydrogen with the hydrogen in the aqueous phase. This would be in agreement with the results and arguments of Bucur (1961) discussed previously concerning measurements of the electrode potential of palladized specimens in mixtures of H_2O and D_2O. However, it does not seem completely consistent with Farkas' observations that the gas evolved from an electrode which had been supersaturated electrolytically with

hydrogen contained no more than 0·1% D_2 even when it had been immersed in 69% D_2O. Similarly, it seems inconsistent that low contents of deuterium were found in the gas evolved through a solution containing 39% D_2O when this was in contact with the "diffusion" side of a palladium bielectrode, whilst virtually pure hydrogen (protium) was being discharged at the "polarization" side. A dependence of the state of activity of the surface on the exchange with solution seems to have been indicated by some experiments of Trusov and Aladzhalova (1960b) involving exchange reactions of both deuterium and tritium at the surface of palladium "bielectrode" membranes.

Recently, studies have been made (Flanagan, 1963; Botter, 1965) into the possibility of obtaining improved separation factors at around room temperature by using, in preference to pure palladium, certain alloys (e.g., with platinum) which can exhibit larger difference in the relative solubilities of the isotopes over experimentally more convenient ranges of pressure as illustrated in Fig. 8.12. Very recently, studies of separation factors using Pd/Ag alloys have been reported by Brodowsky *et al.* (1966).

When surfaces have been suitably activated, a very high percentage

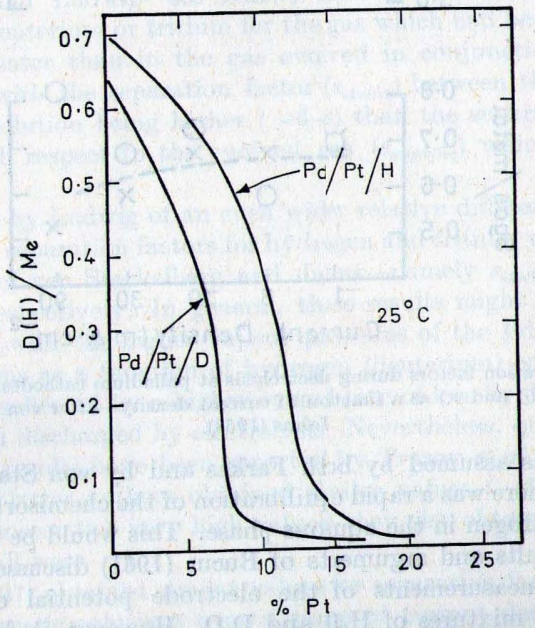


FIG. 8.12 Comparison of the solubility of hydrogen and deuterium as a function of the Pt content in Pd/Pt alloys at 25° under pressuresof ~760 mm Hg—after Maeland and Flanagan (1964).

of the hydrogen discharged electrolytically at fairly low current densities can be absorbed by palladium membranes rather than evolved as gas. This can be a continuous process if the absorbed hydrogen is concurrently removed from the "inner" or diffusion side of the membrane —for example, by oxidation. One conveniently controlled form of oxidation is to make the diffusion side of the membrane the anode of a further electrolytic circuit. This arrangement has been put forward by Salmon (1956) as the basis of a competitive method for the separation of hydrogen isotopes. Salmon's basic unit consisted of a tube-shaped palladium membrane as shown in Fig. 8.13 which, in order to reduce

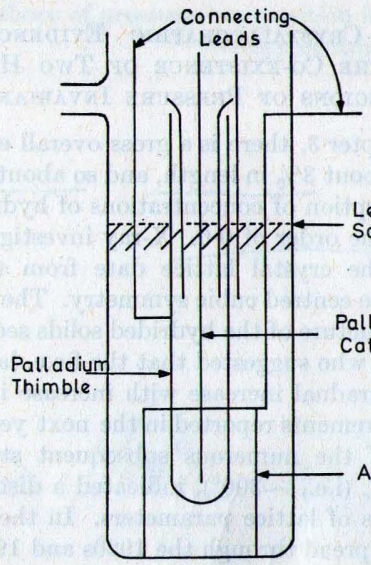


FIG. 8.13 A form of electrolytic cell for separation of hydrogen isotopes—after Salmon (1956).

problems concerning changes of dimensions, was both pre-saturated with hydrogen and fitted into an annulus rather than being firmly attached to gas leads. As already discussed in Chapter 3, some of the problems of deformation can be reduced by using certain palladium alloys such as those which have largely superseded pure palladium for purposes of gas purification. Related studies of separation factors have recently been published by Lauer and Vielstich (1965) and Wicke and Gibmeier (1964).

CHAPTER 9

Investigations of Changes of Lattice Structure and of Some Other Physical and Electrical Properties as Functions of Hydrogen and Deuterium Contents

A. General X-ray Crystallographic Evidence of Lattice Expansion and of the Co-existence of Two Hydride Phases over Regions of Pressure Invariance

As discussed in Chapter 3, there is a gross overall expansion of palladium specimens by about 3% in length, and so about 10% in volume, as a result of the absorption of concentrations of hydrogen equivalent to values of H/Pd of the order of 0·6. X-ray investigations of accompanying changes in the crystal lattice date from the early 1920s. Palladium itself has face centred cubic symmetry. The earliest reported study of the crystal structure of the hydrided solids seems to have been that of Yamada (1922) who suggested that the f.c.c. lattice parameters showed a continuous gradual increase with increase in hydrogen content. However, measurements reported in the next year by McKeehan (1923) and in each of the numerous subsequent studies below the critical temperature, T_c (i.e., ~300°), indicated a discontinuity in the range of derived values of lattice parameters. In the majority of the further investigations spread through the 1920s and 1930s (Krüger and Sacklowski, 1925; Linde and Borelius, 1927; Krüger and Gehm, 1933; Nähring, 1934; Rosenhall, 1933), the hydrogen was introduced into the specimens by electrolysis so that if left in an oxidizing atmosphere at some stage of the X-ray measurements, the hydrogen could possibly have left the specimen spontaneously before the actual determination. Only the measurements of Linde and Borelius and of Rosenhall, who estimated hydrogen contents by outgassing *in vacuo* after each exposure, are reasonably free from this criticism. Nevertheless, all of these studies provided general evidence of a phase transformation as indicated by the appearance of a second set of reflections which could be interpreted as due to a new phase (β-phase) which apparently retained the f.c.c. symmetry of pure palladium, but which exhibited approximately a 3% increase in lattice parameter.

B. Correlation of Lattice Parameters with p–C Relationships and with Hysteresis

A correlation between changes of lattice parameters and equilibrium hydrogen pressures was obtained by Owen and Jones (1937) and by Owen and Williams (1944) (cf. also Owen, 1944) using specimens in the forms of both powder and wire. In these studies, the lattice parameters were recorded after specimens had equilibrated with successive doses of hydrogen at temperatures within the range 60–120°. No measurements were obtained of changes of hydrogen content but plots of lattice parameter against the equilibrium pressure of hydrogen were clearly of a similar form to those of pressure–composition isotherms at comparable temperatures. The plots in Fig. 9.1 representing results at 100° suggest that for regions where there is a gradual increase of equilibrium pressure

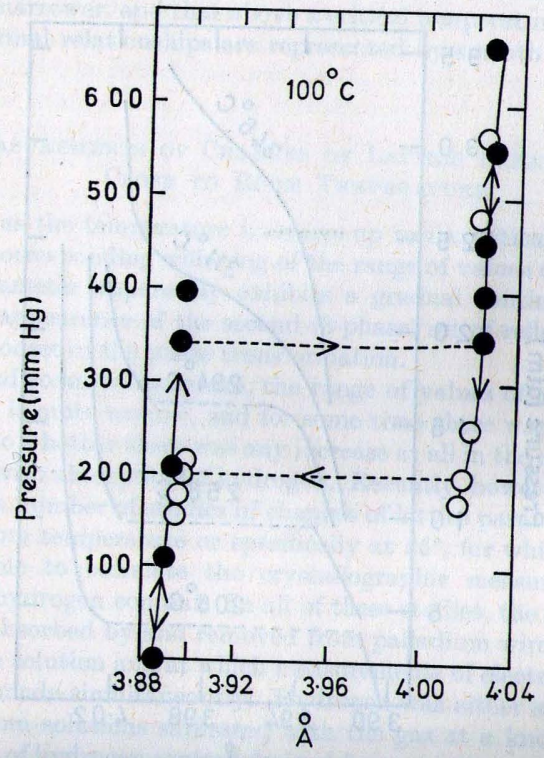


FIG. 9.1 Relationships between f.c.c. lattice constants and "steady-state" pressures during absorption, ●, and desorption, ○, of hydrogen by palladium powder at 100°—after Owen and Jones (1937).

with each dose of hydrogen, there is also a complementary gradual increase in the lattice parameter (i.e., over regions which are designated α-phase in the p–C relationships). However, when a pressure of 340 mm Hg is reached, an additional set of reflections appear which are designated as corresponding to the β-phase hydride. With the addition of further doses of hydrogen the equilibrium pressure remains at ~340 mm Hg whilst the intensity of the reflections characteristic of α-phase become gradually fainter, and simultaneously the intensity of the β-phase lines shows a steady increase.

Lastly, when the reflections characteristic of the α-phase finally disappear, this is paralleled by a rise in the equilibrium vapour pressure, and by a further gradual shift of the position of the β-phase reflections; this shift generally has been interpreted as indicating a further expansion of the f.c.c. lattice constant.

On reversing the sequence and now removing hydrogen from the

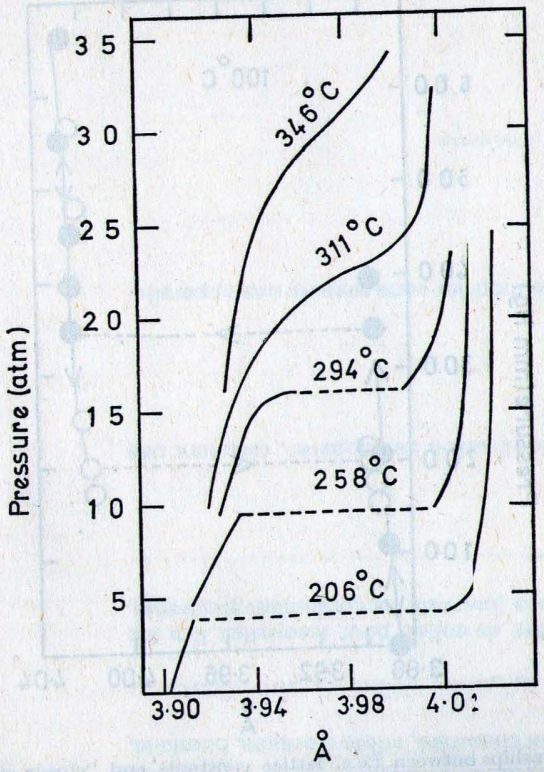


FIG. 9.2 Relationships between lattice constants and steady-state pressures for desorption isotherms—after Maeland and Gibb (1961).

specimen in stages, there is first an apparent reversibility of plots of lattice constant against pressure over purely β-phase regions, but when there is a reappearance of reflections characteristic of α-phase, the equilibrium pressure is found to be only ~210 mm Hg (again at 100°) where it virtually remains over the whole of the β- → α-phase transformation.

More recently, similar sequences of measurements have been carried out by Maeland and Gibb (1961) over a higher range of temperatures from 206–346°. Again only equilibrium values of hydrogen pressure were recorded—no attempts being made to measure complementary changes of hydrogen content. Maeland and Gibb still found evidence of hysteresis at 206°, but the diagram in Fig. 9.2 of their results combined with those of Owen and his colleagues shows a family of curves of similar form to the corresponding p–C isotherms in that the region of discontinuity corresponding with the phase transformation becomes gradually narrower, and that above a critical temperature T_c of ~300°, the isothermal relationships are represented by smooth and reversible curves.

C. Measurements of Changes of Lattice Parameters at Close to Room Temperature

Clearly, as the temperature increases up to the critical temperature, there is a corresponding widening of the range of values over which the lattice parameter apparently exhibits a gradual continuous increase before the appearance of the second (β-phase) set of reflections indicative of the onset of the phase transformation.

At around room temperature, the range of values of α-phase lattice parameters is quite narrow, and for some time there was a measure of dispute as to whether there was any increase at all in the α-phase lattice parameter with absorption of hydrogen. Recently, however, there have been quite a number of studies of changes of lattice parameter either at ambient room temperature or specifically at 25°, for which it has also been possible to correlate the crystallographic measurements with changes of hydrogen content. In all of these studies, the hydrogen has been both absorbed by and removed from palladium wires which were immersed in solution and at which measurements of electrode potential were being made simultaneously. Hydrogen was either spontaneously absorbed from solutions saturated with the gas at a known pressure, and changes of hydrogen content derived from measurements of changes of electrode potential and/or electrical resistance with time (Aben and Burgers, 1962; Maeland and Flanagan, 1964; Axelrod and Makrides,

1964); or else the hydrogen was both introduced and removed by electrolysis and the changes of hydrogen content calculated from the amount of current passed (Axelrod and Makrides, 1964; Vert *et al.*, 1965).

All of these sets of measurements are in broad agreement in suggesting the following sequence of changes (expressed in Å) which are illustrated by Fig. 9.3:

(*a*) For values of hydrogen content up to a value of H/Pd ~0·015 [which constitutes the upper limit of α-phase compositions (Simons and Flanagan, 1965a) and has become generally termed α_{max}], there is a gradual increase of lattice constant from a value of 3·889–3·890 for pure palladium up to 3·893–3·895 at α_{max}.

(*b*) The second set of reflections, corresponding to the β-phase concentration which co-exists with α_{max} over the region of α- → β-phase transformation and is generally termed β_{min}, gives derived values of lattice constant which range from 4·013 up to 4·025 in the study of Vert *et al.* (1965) and in the case of all the other three studies—namely Aben and Burgers, Axelrod and Makrides and Maeland and Flanagan—are in excellent agreement in giving the same value of 4·025 Å.

(*c*) Following the disappearance of the α_{max} reflections when H/Pd ~0·58, results obtained by Aben and Burgers and by Vert *et al.* indicate that the lattice constant corresponding to the β-phase reflections shows a further approximately linear increase with hydrogen content to give values of ~4·040 when H/Pd ~0·7 which corresponds to the hydrogen content in equilibrium with a pressure of ~1 atm H_2.

Even larger shifts of the β-phase lines corresponding with still higher but not precisely known values of hydrogen content have been recorded during cathodization of palladium electrodes by Andrews and Ubbelohde (1959). The corresponding lattice constants have been calculated to have values as high as 4·08 Å.

Vert *et al.* (1965) have obtained quite detailed measurements to show a general reversal of the sequence of changes of lattice parameter during what must be virtualy isothermal removal of hydrogen by anodization at ambient room temperature. Aben and Burgers also have shown that α-phase reflections can reappear on partial removal of hydrogen (as the result of exposure to the atmosphere) of a specimen which had been fully transforned to a β-phase composition. Both sets of observations are in keepingwith the findings of Barton *et al.* (1963a) that the lattice parameter reurned to a value characteristic of pure palladium after removal of al hydrogen by oxidation at 25°—and so seem to refute earlier suggesions that the lattice parameter of the hydrogen-free specimen coulc remain at a value corresponding to a β-phase composition (see also Chapter 5).

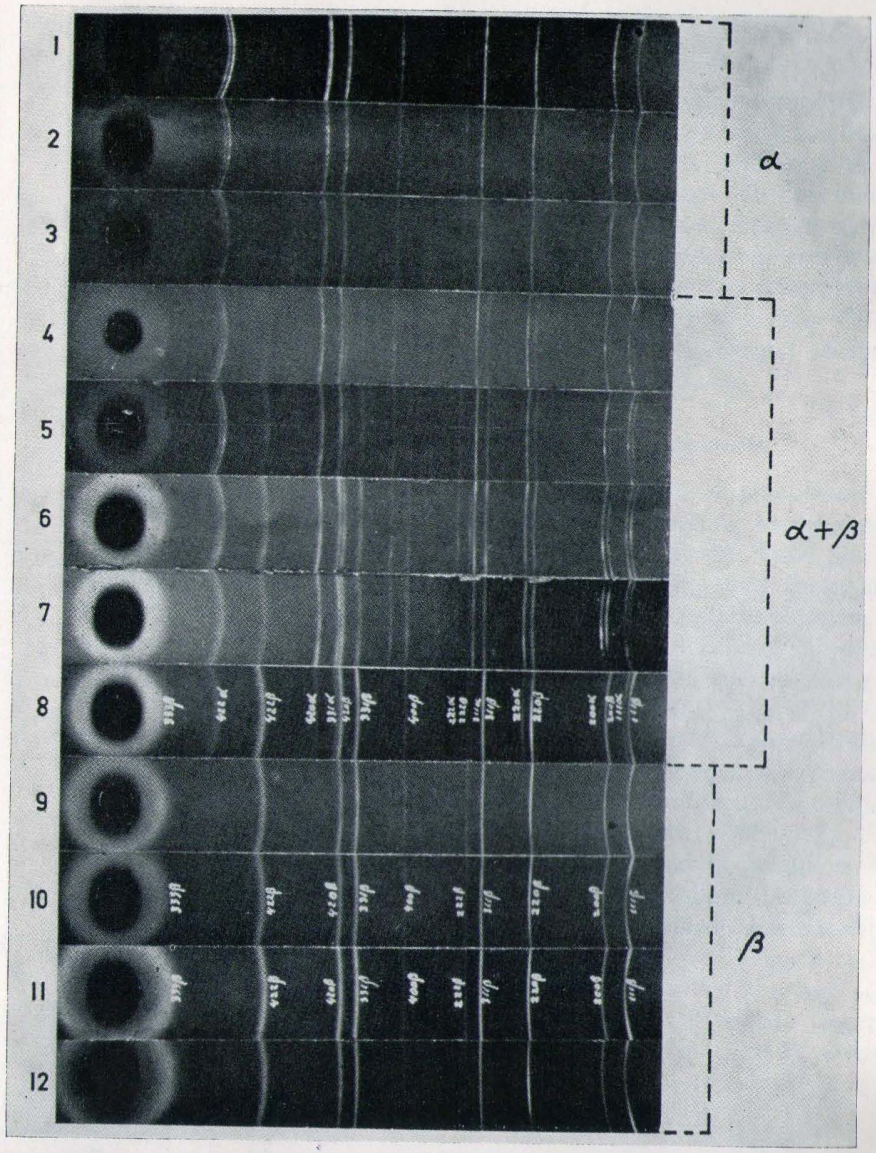


FIG. 9.3 Succession of X-ray powder photographs as a function of increasing hydrogen content at 25°, showing the gradual transition from α- to β-phase compositions. Reproduced by permission of Professor W. G. Burgers and of the Faraday Society.

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D. Changes of Lattice Parameters in the Palladium/Deuterium System

In analogous measurements during the absorption of deuterium by palladium at 25°, Maeland and Flanagan (1964) have recently found the values of lattice parameters for α_{Dmax} to be 3·893 Å, and β_{Dmin} to be 4·027 Å. Although it is perhaps not completely outside the stated margins of error (±0·001 Å), the value for β_{Dmin} compared to the corresponding value for hydrogen (i.e., 4·025 Å) would seem to reflect a somewhat larger relative expansion of the lattice by the deuterium—particularly since the corresponding deuterium content at β_{min} (D/Pd ~0·56) is slightly less than the corresponding hydrogen content (H/Pd ~0·58).

E. Line-broadening of X-ray Reflections

It has been generally observed that the reflections characteristic of the β-phase hydride exhibit considerable line-broadening as compared to those of the original palladium specimen. Moreoever, Laue photographs of β-phase hydrides formed from specimens of a large crystallite size have been found (Sugeno and Kawabe, 1957) to exhibit asterism of a similar form to that found with specimens which had been subjected to extensive mechanical cold working. Again, after specimens have been completely transformed to β-phase hydrides and then all of the hydrogen removed again, the lattice reflections were left considerably broadened compared to those of the original hydrogen-free specimen, although the value of the lattice parameter calculated from the median position had returned to its original value (Barton *et al.*, 1963a).

Removal of line-broadening and asterism required specimens to be annealed at 450–600° which are similar ranges of temperature to those required to anneal mechanical hardness back to values characteristic of very well annealed palladium specimens before any absorption of hydrogen. As has also been stated in a recent review by Maeland and Flanagan (1966), the origin of the line broadening is still in some dispute. Owen (1944) has favoured the view that it is the reflection of a very small crystallite size, but Sugeno and Kawabe have argued that it is caused by general lattice strain and distortion.

F. X-ray Crystallographic Studies of the Absorption of Hydrogen by Alloys of Palladium

So far, X-ray studies of the changes of the lattice parameters of palladium alloys following absorption of hydrogen have been confined

to measurements at or close to ambient room temperature. Generally, the hydrogen has been introduced into specimens by either electrolysis or spontaneous absorption from hydrogen-saturated solutions. Latterly, measurements of electrode potential and/or electrical resistance have been made in conjunction so that the changes of lattice parameter could be correlated with p–C relationships as discussed above for the Pd/H system. As yet, results have been reported only for the Pd/Ag/H, Pd/Au/H and Pd/Pt/H(D) systems in addition to a series of measurements with one Pd/Cu alloy.

The interpretation of the X-ray powder photographs for both the hydrogen-free and the hydrided alloys have been based on the assumption of a retention of f.c.c. symmetry by the metal atoms.

Alloys with lower contents of Au, Ag, Pt (Fig. 9.4) and of 10% Cu (Vert *et al.*, 1965; Tverdovskii *et al.*, 1959a) have been found to exhibit a similar sequence of changes of lattice parameter with increasing

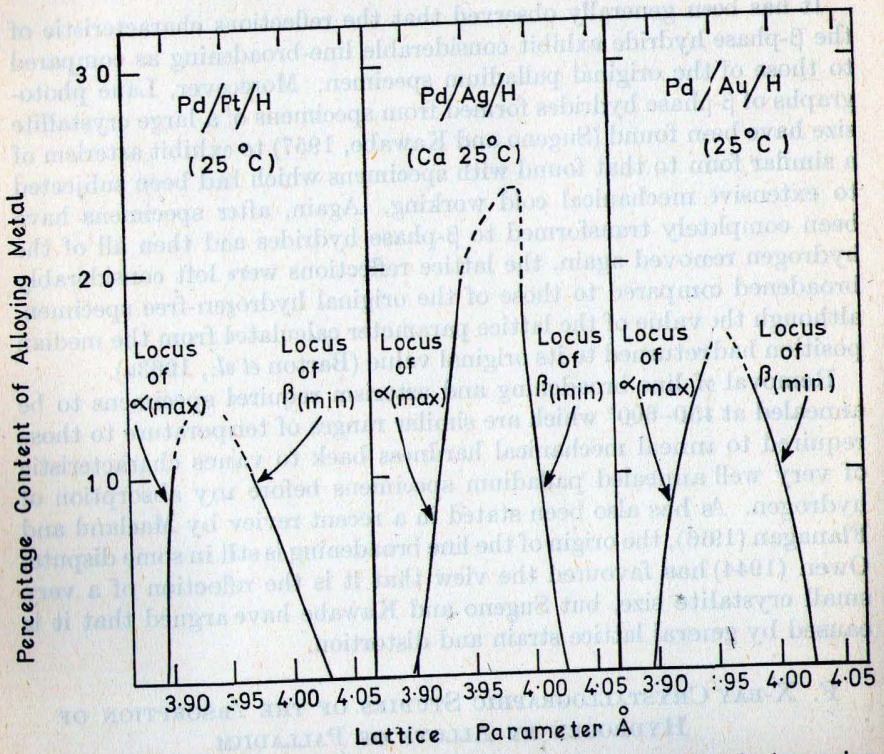

FIG. 9.4 Changes of lattice parameters corresponding with α_{max} and β_{min} for increasing contents of alloying metal—after Maeland and Flanagan (1964), Axelrod and Makrides (1964), Tsuchida (1963), Brodowsky and Poeschel (1965), Maeland and Flanagan (1965).

hydrogen content to relationships for pure palladium, i.e. (1) a gradual increase in lattice parameter over α-phase regions; (2) the appearance of β-phase reflections (β_{min}) and their co-existence with α_{max} reflections over the duration of the α- → β-phase transition which can be indicated by a period when, for example, electrode potential remains virtually invariant with increasing hydrogen content; and (3) a further increase in the β-phase parameter after completion of the α- → β-phase transformation—at least in the case of silver alloys (Axelrod and Makrides, 1964), gold alloys (Maeland and Flanagan, 1965) and a 10% copper alloy (Vert *et al.*, 1965) which are the only systems for which results in this range of hydrogen contents have so far been reported.

With increases in the contents of either silver, gold or platinum, however, the hydrogen content of the β-phase composition corresponding to β_{min} exhibits a gradual decrease (25°) which is paralleled by a gradual reduction in the difference between the lattice parameters characteristic of α_{max} and β_{min}. This tendency is illustrated in Fig. 9.4 and confirms the indications of the corresponding p–C relationships (see Chapter 6) that above certain contents of alloying element sharp phase transformations will no longer occur.

G. X-ray Evidence for Analogous β-phase Hydrides of Nickel

Recently, evidence has been reported from both X-ray and electron diffraction studies (Janko, 1960; Janko and Michel, 1960; Boniszewski and Smith, 1961; cf. also Palczewska and Frackiewicz, 1966) of the formation of hydrides of nickel which are analogous to the β-phase hydride of palladium. These nickel hydrides have been formed from nickel cathodes during electrolysis in solutions containing thiourea. Lattice constants of 3·71 Å and 3·83 Å have been calculated for these hydrides compared to a value of 3·52 Å for pure nickel.

H. Neutron Diffraction Studies and the Location of Hydrogen in the Crystal Lattice

From considerations of changes of density in conjunction with X-ray measurements, Krüger and Sacklowski (1925) calculated that the absorption of hydrogen did not proceed by the actual replacement of palladium atoms by hydrogen, and latterly it has generally been accepted that in the β-phase hydrides, the hydrogen is accommodated into the interstices between the palladium atoms.

In the f.c.c. lattice the interstices are of two types, namely, "tetrahedral" and "octahedral" in which an interstitial hydrogen atom would have four and six nearest palladium neighbours, respectively.

X-ray crystallographic measurements alone were not decisive in deciding which type of interstice was more likely to be occupied in view of the low scattering power of the hydrogen. Neutron diffraction measurements of β-phase hydrides (Worsham *et al.*, 1957; Bergsma and Goedkoop, 1960) and deuterides (Worsham *et al.*, 1957), however, have indicated that at room temperature it is the octahedral positions which are occupied. This corresponds with the hydride having a basically sodium chloride type structure (similar conclusions have been drawn in the case of the β-phase nickel hydride by Wollan *et al.*, 1963). Quite recently, further neutron diffraction studies by Ferguson *et al.* (1965) have been interpreted as indicating that at temperatures $<55°$ K, there is a partial migration of some of the hydrogen from octahedral into tetrahedral sites, and it has been held that this constitutes a satisfactory explanation for complementary changes of heat capacities and electrical resistance which have been discussed in Chapters 2 and 4.

The amplitude of vibration of the hydrogen atoms in the interstices can also be calculated from the neutron diffraction measurements, and there is good agreement between values reported at *ca* 20° by Worsham *et al.* (1957) —0·23 Å; Ferguson *et al.* (1965) —0·25 Å, and also by Bergsma and Goedkoop (1960) who obtained a value of 0·24 Å by the neutron diffraction technique. Their findings were confirmed with neutron transmission and by incoherent neutron scattering measurements—from the latter of which they calculated a vibration amplitude of 0·22 Å. Worsham *et al.* (1957) have found the vibration amplitude of deuterium in the β-phase deuteride at room temperature to be rather lower (0·20 Å) than that of hydrogen in the hydride, and Ferguson *et al.* (1965) have recently reported that the amplitude of vibration of hydrogen is still as high as 0·17 Å at 4·2° K.

I. Location of the Hydrogen in α-phase Hydrides

So far, it has not been possible to locate the position of the hydrogen in the α-phase hydrides from neutron diffraction studies. However, for some time the X-ray crystallographic interpretation of an apparent gradual increase of the mean f.c.c. lattice parameter with increasing hydrogen content has rather diverted attention from consideration of dimensional changes around each particular hydrogen atom. Nevertheless, it has been argued (Lewis, 1961b; also von Stackelberg and Ludwig, 1964) that the immedately neighbouring palladium atoms are

likely to retract to new relative positions which are likely to be little different from those around an occupied interstice in the β-phase lattice.

J. Face-centred-cubic Symmetry and Lattice Vacancies in β-phase Hydrides

If the conclusions of the neutron diffraction studies are accepted, that the β-phase hydride has a sodium chloride structure, there must generally be numerous vacancies in the hydrogen lattice. It would seem reasonable to suppose that there will be local contractions of palladium atoms into these vacancies. Maeland and Gibb (1961) have suggested that the gradual apparent increase of the β-phase lattice parameter with increasing hydrogen content is a reflection of a gradual expansion of the average lattice constant out towards a theoretical limit corresponding to a hypothetical stoichiometric 1:1 ratio of hydrogen to palladium and which may possibly be approximately representative of the actual bond distances around an occupied interstice at any value of hydrogen content.

K. Changes of Magnetic Susceptibility as a Function of Hydrogen Content

Pure palladium is markedly paramagnetic with a value of χ_A of $\sim 550–600 \times 10^{-6}$ c.g.s. units.

Subsequent to the work of Biggs (1916), a number of experimental studies have been made of the changes of magnetic susceptibility upon absorption of hydrogen, and all are in general agreement that there is a virtually linear decrease of paramagnetism with increasing hydrogen content as indicated by Fig. 9.5.

There are some relatively minor differences of the exact form of the relationships: the measurements of Aharoni and Simon (1929) (in which the hydrogen was introduced into the palladium from the gas phase) gave slightly lower values of magnetic susceptibility than the results of Biggs and also those of Svensson (1933) (where in both cases the hydrogen had been introduced into the specimens by electrolysis). The relationships, however, between χ_A and hydrogen content had virtually the same gradient. A further comprehensive series of measurements was carried out by Sieverts and Danz (1937) (again specimens were loaded with hydrogen by electrolysis) who, although also recording lower values of χ_A over low ranges of hydrogen content than either Biggs or Svensson, obtained good agreement with these authors for the value (H/Pd $\sim$0·65 at 18–22°) of hydrogen content at

which the solids became diamagnetic. Sieverts and Danz (1937) also found that the effects of adding deuterium were virtually quantitatively identical to those of hydrogen. Latterly, some measurements

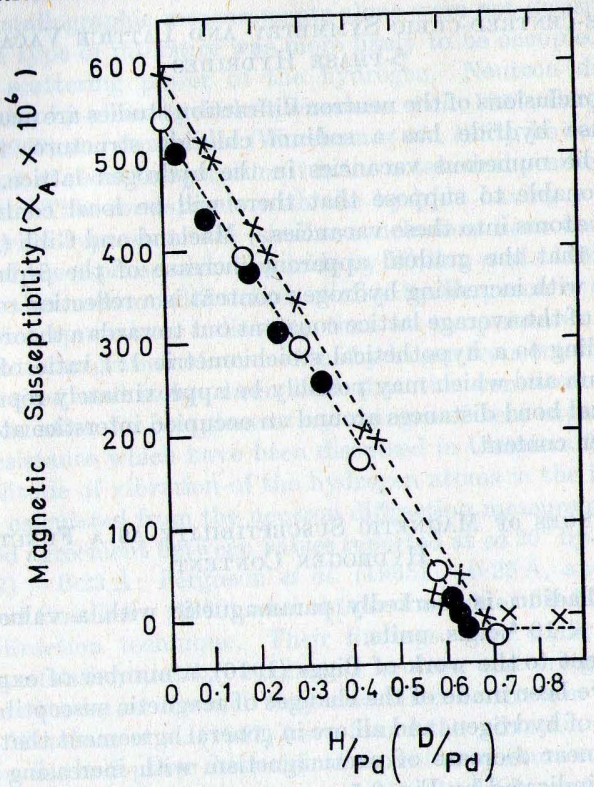

FIG. 9.5 Comparison of relationships between magnetic susceptibility and hydrogen content as derived by Svensson (1933), ×, at 18°; and magnetic susceptibility and both hydrogen, ○, and deuterium, ●, contents derived by Sieverts and Danz (1937), (18–22°).

exhibiting a broadly similar trend have been obtained at lower temperatures by Wucher (1952) and analogous decreases of magnetic susceptibility upon absorption of hydrogen have been reported for some palladium/nickel alloys by van Loef (1963) and for some palladium/silver alloys by Tsuchida (1963). [See also Furger *et al.* (1959) in reference to some studies with palladium/iron alloys].

As yet, no comprehensive measurements have been made of the changes of magnetic susceptibility during desorption of hydrogen; but, fairly recently (Barton *et al.*, 1963a), it has been shown (in contradiction of earlier reports by Michel and Michel, 1945) that, even at room

temperature, the magnetic susceptibility returns to close to the value for pure palladium upon complete isothermal removal of hydrogen.

L. Changes of Other Electrical Properties of Palladium and Palladium Alloys as a Function of Hydrogen Content

1. *Surface Properties*

Changes of photoelectric sensitivity and thermal emissivity of electrons following absorption of hydrogen have been reported by Nübel (1931), Wortmann (1933) and Schneidermann (1935) for series of palladium/silver and palladium/gold alloys, but generally at only one value of hydrogen content for each alloy. Moreover, this composition has not been the same for each alloy but corresponds to the "maximum" amount of hydrogen which could be introduced into the alloy by electrolysis. Generally, however, a plot of the parameter against gold or silver content for these hydrided solids continued to exhibit maxima at gold or silver contents which were not far removed from the maxima in the analogous relationships for the hydrogen-free alloys. More recently, the photoelectric sensitivity of palladium films at −80° and −195° has been shown by Suhrmann *et al.* (1964) to decrease substantially with increasing hydrogen content.

2. *Hall Coefficient*

The Hall Coefficient of pure palladium seems to be virtually unaltered by changes of hydrogen content (Raethjen, 1924).

Slight decreases in the Hall Coefficients of palladium/silver and palladium/gold alloys following absorption of hydrogen have been reported by Wortmann (1933) but, again, measurements were obtained at only one content of hydrogen for each alloy. More recently, Tsuchida (1963) has found the Hall Coefficient of a palladium alloy with 15% silver to exhibit only minor decreases over a relatively wide range of hydrogen contents, although somewhat more marked decreases were recorded for a 30% Ag alloy—particularly at higher hydrogen contents.

3. *Thermoelectric Power*

The thermoelectric power of palladium is quite substantially altered by absorption of hydrogen.

In measurements by Knott (1866) and Heimberg (1923) changes of the hydrogen content of specimens were estimated from concurrent measurements of electrical resistance. Whilst they were not in complete quantitative agreement, both studies indicated that the effect of

absorption of hydrogen was to make the thermoelectric power considerably more positive in terms of the absolute scale of this parameter with respect to lead. Thus, at 18°, Fig. 9·6 indicates that thermo-

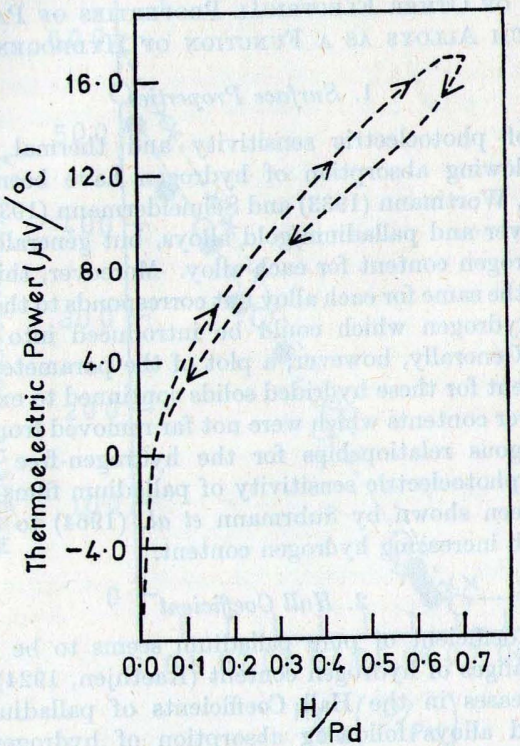

FIG. 9.6 Changes of absolute thermoelectric power as a function of hydrogen content at *ca* 18° as estimated from measurements of Heimberg (1923).

electric power increases from a value of ~−6·8 mV/° for pure palladium up to values of the order of 16·0 or 18·0 mV/° at β-phase concentrations where H/Pd ~0·7. Some measurements of changes of the thermoelectric power of Pd/Ag and Pd/Au alloys reported by Nübel (1931) and Schneidermann (1932) also indicate an overall shift to positive values, but again have been made at only one value of hydrogen content for each alloy.

More recently, measurements with palladium wires have been reported by Schindler *et al.* (1959) over a lower range of temperatures from 10 to 110° K. Figure 9.7 illustrates that for specimens with higher hydrogen contents, the relationships exhibit a shallow minimum over a

range of temperatures closely similar to those where there is a maximum in the plots of specific heat against temperature and—for specimens of comparably high hydrogen contents—in plots of electrical resistance

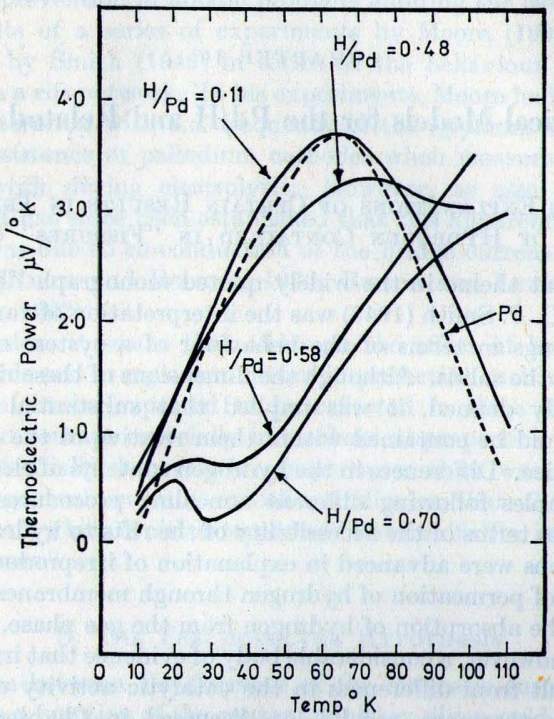

FIG. 9.7 Changes of absolute thermoelectric power at low temperatures for specimens with differing hydrogen contents—after Schindler *et al.* (1959).

against temperature (see Fig. 4.6). Preliminary measurements of changes of the thermo-electric power of palladium films at very low contents of hydrogen have recently been reported by Eley and Petro (1966).

CHAPTER 10

Theoretical Models for the Pd/H and Related Systems

A. Possible Explanations of Certain Results in Terms of the Behaviour of Hydrogen Contained in "Fissures" or "Rifts"

A dominant theme in the widely quoted monograph "Hydrogen in Metals" by D. P. Smith (1948) was the interpretation of various experimental findings in terms of the behaviour of a system of "rifts" or "fissures" in the solids. Although the dimensions of these rifts were not quantitatively defined, it was implied that substantial volumes of hydrogen could be contained within them relative to the solubility in the bulk lattice. Differences in the hydrogen contents of electrolytically charged samples following different annealing procedures have been interpreted in terms of the accessibility of the rifts to hydrogen. Allied interpretations were advanced in explanation of irreproducibility both of the rates of permeation of hydrogen through membranes, and of the kinetics of the absorption of hydrogen from the gas phase.

There is, however, a considerable body of evidence that irreproducible kinetics result from differences in the catalytic activity of the metal surfaces. Furthermore, results, as discussed in Chapters 2 and 6, indicate that where there is good evidence of the establishment of true thermodynamic equilibrium, solubilities have been found to be virtually independent of the grain size and general degree of annealing of specimens—or even of whether they are in a finely particulate form as prepared by chemical precipitation.

Certain other experimental findings described as "overstepping phenomena" have also been interpreted by Smith in terms of the behaviour of rift networks. These oversteppings refer to certain changes of the electrode potential, electrical resistance and external dimensions of palladium electrodes after alteration or cessation of the current density of electrolysis. However, as discussed in a recent resurvey of overstepping phenomena (Barton *et al.*, 1966c), the experimental evidence cited by Smith now seems rather meagre. No analogous effects have been observed in any of the generally more comprehensive subsequent studies of changes of electrical resistance or electrode potential

which could not be attributed to alternative reasons such as hysteresis of the relationships, or a delayed establishment of equilibrium between the concentrations of hydrogen at the surface and in the interior, or the incomplete prevention of anodic products entering the catholyte.

The results of a series of experiments by Moore (1939) also were interpreted by Smith (1948) in terms of the behaviour of hydrogen contained in a rift network. In his experiments, Moore had observed an apparent alteration with a.c. frequency of the apparent values of the electrical resistance of palladium cathodes when measured by an a.c. bridge network during electrolysis. However, as also discussed in Chapter 4, it has since been established that this apparent "spread" of resistance was due to co-conduction of the bridge current through the electrolyte (Knorr and Roemer, 1960; Barton and Lewis, 1962a; cf. also Harvey, 1962).

In conclusion, it seems that although the effect of hydrogen contained in voids and in regions of lattice imperfection such as dislocation networks, might be expected to be reflected in some differences in physical, and perhaps especially in mechanical properties, these effects are of substantially less relative importance than was believed by Smith. In general, current evidence indicates that the more pronounced effects which Smith interpreted in terms of rifts, have been due to other causes.

B. The Pseudo-silver Hypothesis

Similarities between the decrease of the magnetic susceptibility of palladium as a function of the content of either silver, gold or hydrogen led to suggestions by Oxley (1922) and Vogt (1932) that interaction between the hydrogen and specific palladium atoms or ions could yield Pd/H (or Pd/H^+) entities which could be considered as equivalent to an equal number of Ag atoms (or ions). A virtual equivalence between Ag atoms and such Pd/H entities also has been suggested by Rosenhall (1935) in his interpretation of X-ray crystallographic studies of the Pd/Ag/H system. The proposed Pd/H entity would be isoelectronic with silver but, on the other hand, it would be binuclear so that an exact interchangeability could hardly be expected under all conditions.

Nevertheless, some additional encouragement for a simple correlation between Pd, H and Ag has been given by the citing of evidence that the solubility of hydrogen in Pd/Ag alloys can decrease more or less linearly with silver content. However, when the citing of the solubility of hydrogen is more rigorously defined with reference to the pressure of hydrogen gas in equilibrium, it is found, as discussed in Chapter 6, that

any approximation to a linear dependence of hydrogen solubility on silver content, seriously breaks down over substantial ranges of reference pressure.

C. The Possibility that Hydrogen is Dissolved as Protons

An extension of the pseudo-silver hypothesis was to accept that the hydrogen was probably located fairly centrally in interstitial positions without being specifically bound to a particular palladium atom, and to primarily consider the effects of the electrons from the added hydrogen or silver on the electronic structure of palladium.

Until quite recently, it had been accepted from the magnitude of the paramagnetism of palladium that there were 0·6 holes or vacancies per atom in its "4d" band; and it had been proposed (Mott and Jones, 1936) that, for values of H/Pd up to ~0·6, these vacancies were filled by electrons from the hydrogen. However, in order to cope with the fact that H/Pd could on occasion exceed 0·6, it had to be proposed that the complementary additional electrons were incorporated into the "5s" band (Lacher, 1937). As a further complication to a simple correlation, the most recent theoretical analysis of the palladium band structure now suggests that there are only 0·36 holes in the "4d" band per palladium atom (Vuillemin and Priestley, 1965; Dugdale and Guénault, 1966). In an associative way, the presence of the hydrogen as protons provides an analogy with the alloying properties of silver which is further encouraged by the retention of excellent thermal and electrical conductivity and workable malleability. The analogy also provides a historical link with Graham's original proposal that the hydrogen was behaving as if it was an alloying metal—in which capacity it should be given a separate title, namely hydrogenium.

Indeed it has been pointed out (Ubbelohde, 1937) that formal calculations of the internal pressure, commensurate with the expansion in volume resulting from the formation of the β-phase, yield values of a similar order of magnitude ($\sim 2{\cdot}5 \times 10^5$ Kg/cm^2) to the pressures at which theoretical calculations have suggested that hydrogen could be transformed to a metallic allotrope. An objection to this analogy could be that the relative positions of the hydrogen atoms in palladium must be very different from those in the hypothetical metallic form of pure hydrogen. Other theoretical discussions and calculations concerning the general possibility that hydrogen absorbed by other transition metals as well as palladium is ionized to form protons have been published at intervals (Franck, 1933; Herzfeld and Goeppert-Mayer, 1934; Isenberg, 1952). Further experimental evidence suggesting that

the absorbed hydrogen exists as protons seems to be provided by the measurements of Wagner and Heller (1940) which seemed to indicate an apparent transport of hydrogen as a positively-charged species under the influence of an applied electric field as discussed in Chapter 7.

On the other hand, since the invoking of the pseudo-silver and proton gas theories, there has latterly been increasing evidence that it is a very widespread or even general characteristic of chemical systems to exhibit families of p–C isotherms which are analogous to those of the Pd/H system in indicating the existence of solid phases of non-stoichiometric composition.

Furthermore, even when the components of these systems comprise a non-metallic element such as oxygen or sulphur in addition to a metal, the solid phases may still retain substantial metallic characteristics. Perhaps the closest analogies with the Pd/H system are provided by the binary systems with hydrogen and other transition metals from Groups 3, 4 and especially Group 5 (namely vanadium, niobium and tantalum). Here, despite a greater tendency for these metals to disrupt on the formation of a hydride, there is still a retention of considerable electrical conductance; and in addition to similarities in the form of p–C relationships, there are also similarities between nuclear magnetic resonance absorption spectra. From considerations of changes of lattice parameters it has been suggested that the hydrogen in these latter solid hydrides could be in the form of negative rather than positive ions (Libowitz and Gibb, 1956; Gibb and Schumacher, 1960) so that a correlation of the various lines of evidence seems to raise at least a possibility that this could also be the case for hydrogen in palladium.

D. The Possibility of Ordering to More Covalent Molecular Units at Very Low Temperatures

It has been advanced by Aston and colleagues that the specific heat anomalies in the region of 55° K, which have been referred to in Chapters 2 and 8, could be associated with the formation of PdH_4 molecular units at low temperatures. This inference was suggested by analogy with specific heat anomalies of a similar type which had been attributed to cooperative rotational transitions in the cases of NH_4^+ and CH_4. Either a tetrahedral (Nace and Aston, 1957) or a square coplanar (Mitacek and Aston, 1963) coordination of the hydrogen around the palladium has been suggested. When H/Pd exceeded about 0·5, it was also argued by Mitacek and Aston that the square coplanar arrangement could give rise to fairly extensive continuous

planes of hydrogen atoms which, it was suggested, would partly limit conduction and so account for the rather high values of electrical resistance of these compositions at temperatures <55° K, as referred to in Chapter 4.

Some support for an adoption of tetrahedral coordination also seems to be indicated by recent neutron diffraction studies of β-phase hydrides at low temperatures by Ferguson *et al.* (1965). Their interpretation was that there is a partial migration of hydrogen from octahedral to tetrahedral interstices, which they also advanced could be accountable for both the specific heat anomalies and for the changes of conductivity. Finally, it has also been pointed out (Lewis 1962a) that if the specific heat anomaly was associated with a rotational transition, this could possibly refer to bonds formed between pairs of adjacent hydrogen atoms.

E. Theoretical Derivation of p–C Relationships

Perhaps the first attempts to derive theoretical equations which could be correlated with experimentally determined p–C–T relationships was due to Fowler and Smithells (1937) using the methods of statistical thermodynamics. For many metals which absorb relatively little hydrogen such as copper, cobalt and platinum, experimental information was, and generally still is, limited to a knowledge of solubility under a pressure of one atmosphere as a function of temperature. There is, however, a virtually linear relationship between the logarithm of hydrogen solubility and $\frac{1}{T}$ over appreciable ranges of temperature. Fowler and Smithells equated free energies derived from the partition functions of the hydrogen in the metal and in the gaseous phase in equilibrium and partly because it was an advantage in simplifying the analysis, made a final assumption that the hydrogen was absorbed as protons. They derived an equation of the form

$$\log\,(\text{hydrogen content}) = \text{constant} - \frac{I + \chi_p - \chi + \frac{1}{2}\chi_d}{kT} \qquad (10.1)$$

where I is the ionization energy of hydrogen atoms, χ_p was the energy of solution of the protons, χ the thermionic work function of the metal and χ_d the dissociation energy of hydrogen molecules.

Quite soon afterwards, an extension of this general approach to the case of the Pd/H system was published by Lacher (1937). Lacher retained the assumption that the hydrogen was absorbed as protons but, to allow for the possibility of the formation of a second (β-)phase,

added an additional premise that the absorbed protons attracted one another with an interaction energy χ (also alternatively termed by other authors E_H, W_{HH}, W_{aa} and E†) of an unspecified nature. Lacher's analysis led to an equation between the equilibrium vapour pressure of hydrogen, p, temperature and hydrogen content of the form

$$\log p^{\frac{1}{2}} = \log \frac{\theta}{1-\theta} - \frac{(\chi_0 - \frac{1}{2}\chi_d + \theta\chi)}{kT} + \text{const} \qquad (10.2)$$

where χ_0 is the energy of the absorbed hydrogen with respect to its lowest quantum state in the gas phase. This form of equation gives a

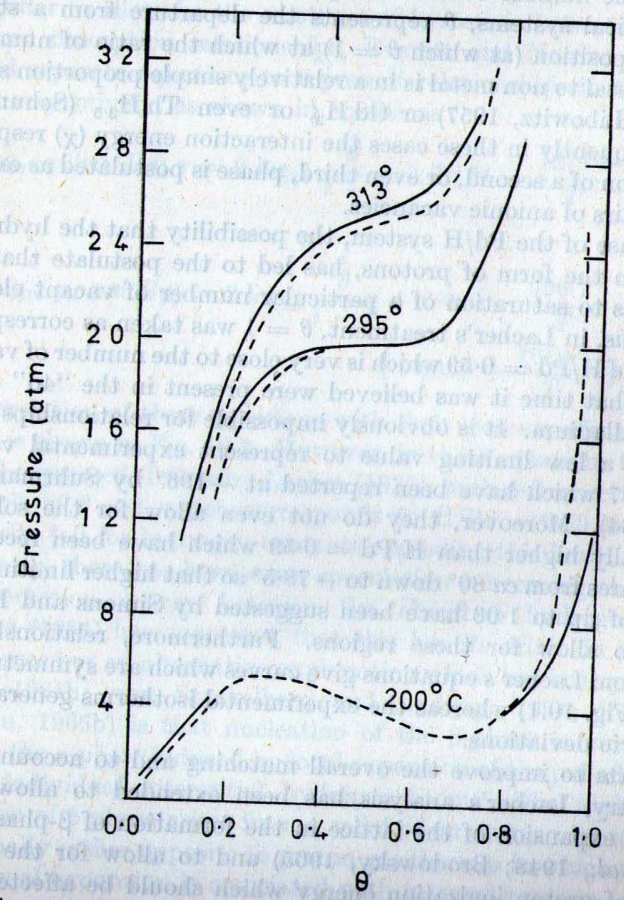

Fig. 10.1 Diagrammatic reproduction of Lacher's (1937) comparison of p–C relationships of Gillespie and Galstaun (1936) (continuous lines), with theoretically derived relationships (broken lines)—where θ equals H/Pd/0·59.

relationship between p and θ which has the shape of a critical isotherm when $T = \chi/4k$, and at lower temperatures has three roots as shown, for example, by diagrammatic relationships in Fig. 10.1.

Subsequently, equations of a related form also have been derived (Anderson, 1946; Rees, 1954a, b; Libowitz, 1957; Anderson and Barraclough, 1963; Schumacher, 1964; Hyde *et al.*, 1966) to represent the p–C–T relationships of other chemical systems which show deviations from stoichiometry. The extent of the deviations is reflected by the value of θ [or an equivalent term such as n/N_s (Wicke and Nernst, 1964; Simons and Flanagan, 1965b) where n is the number of occupied sites and N_s is the number of sites occupied at saturation]. In models of other chemical systems, θ represents the departure from a stoichiometric composition (at which $\theta = 1$) at which the ratio of numbers of atoms of metal to non metal is in a relatively simple proportion such as, e.g., UH_3 (Libowitz, 1957) or GdH_3, or even $ThH_{3\cdot5}$ (Schumacher, 1964). Frequently in these cases the interaction energy (χ) responsible for formation of a second, or even third, phase is postulated as exercised between pairs of anionic vacancies.

In the case of the Pd/H system, the possibility that the hydrogen is absorbed in the form of protons, has led to the postulate that $\theta = 1$ corresponds to saturation of a particular number of vacant electronic levels. Thus, in Lacher's treatment, $\theta = 1$ was taken as corresponding to a value of H/Pd = 0·59 which is very close to the number of vacancies which at that time it was believed were present in the "4d" electron band of palladium. It is obviously impossible for relationships derived with such a low limiting value to represent experimental values of H/Pd ~1·7 which have been reported at −196° by Suhrmann *et al.* (1959, 1964). Moreover, they do not even allow for the solubilities substantially higher than H/Pd = 0·59 which have been recorded at temperatures from *ca* 80° down to −78·5° so that higher limiting values of H/Pd of up to 1·00 have been suggested by Simons and Flanagan (1965b) to allow for these regions. Furthermore, relationships calculated from Lacher's equations give curves which are symmetric about $\theta = 0{\cdot}5$ (Fig. 10.1) whereas the experimental isotherms generally show asymmetric deviations.

In efforts to improve the overall matching and to account for the assymmetry, Lacher's analysis has been extended to allow for the effects of expansion of the lattice in the formation of β-phase (Harashima *et al.*, 1948; Brodowsky, 1965) and to allow for the effect of changes of proton ionization energy which should be affected by the state of occupation of vacant levels and the electronic band shape (Simons and Flanagan, 1965b; Brodowsky, 1965). The amended

equations lead to an improved correspondence with the experimental relationship over certain ranges of temperature and pressure, and Simons and Flanagan have obtained a satisfactory correlation between their theoretical relationships and trends in the experimental relationships between heats of absorption of hydrogen and hydrogen content.

Nevertheless, some differences between all of the modified theoretical relationships and the experimental p–C isotherms have still remained. For example, in the case of studies by Harashima *et al.* (1948), the modifications have not resulted in quite such a good parallel improvement in the matching of theoretical and experimental relationships in the case of the Pd/D system (Tanaka *et al.*, 1948).

In order to allow for the existence of hysteresis between the absorption and desorption relationships, Everett and Nordon (1960) have derived separate equations to represent relationships in the α- and β-phase, respectively, as shown in equations

$$\log_{10} p_\alpha(cm\ Hg)\ \gamma = 2 \log_{10} \frac{\theta}{1-\theta} + 7{\cdot}164 - \frac{1277{\cdot}6}{T} - \frac{1973{\cdot}9}{T}\theta \tag{10.3}$$

and

$$\log_{10} p_\beta\ (cm\ Hg) = 2 \log_{10} \frac{\theta}{1-\theta} + 6{\cdot}669 - \frac{996{\cdot}7}{T} - \left(0{\cdot}6058 + \frac{1629{\cdot}7}{T}\right)\gamma \tag{10.4}$$

The correlation of these equations with their own experimental results at 120° is shown in Fig. 10.2. However, in these equations the value of θ is still expressed, following Lacher (1937), with reference to a saturation limit of $\theta = 1$ which corresponds to H/Pd = 0·59 and so must necessarily fail for hydrogen contents exceeding this limit.

Recently, there has been some speculation concerning the source of the interaction energy between the absorbed hydrogen entities. Makrides (1964) has suggested that this has its origin in rather long range forces but an alternative explanation which has been put forward (Lewis, 1961b; von Stackelberg and Ludwig, 1964; Simons and Flanagan, 1965b) is that nucleation of the β-phase is motivated by strain in the α-phase induced by local expansion of the palladium atoms around individual interstitial hydrogen atoms. The idea that the nucleation of β-phase arises from a relief of strain may be regarded as conceptually rather opposite to proton gas theories in which the overall dimensional expansion is associated with internal pressure.

At present in general, incomplete knowledge of the reason for the expansion of the lattice and of the form in which the hydrogen is

absorbed hinders application of an analysis of the energetics of lattice formation in terms of modified forms of Born–Haber cycles—such as has been attempted by Gibb (1962a) in the case of hydrides for which

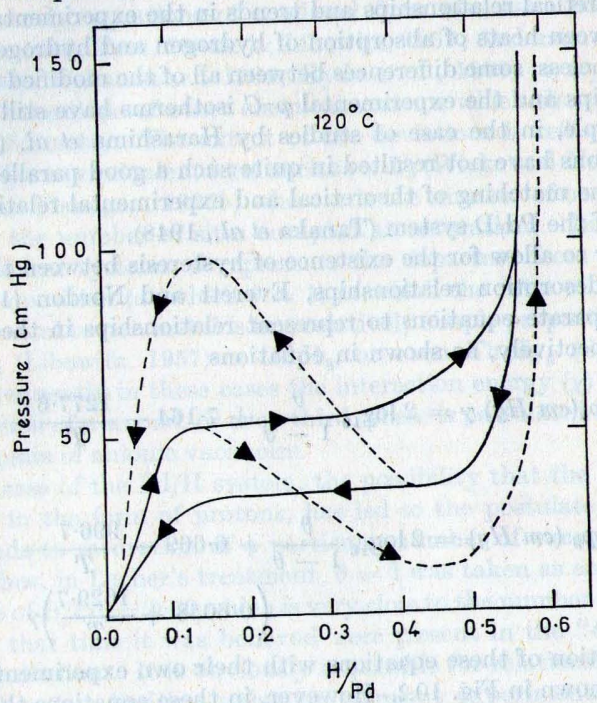

FIG. 10.2 Comparison of both absorption and desorption p–C relationships at 120° with corresponding theoretical relationships (broken lines)—after Everett and Nordon (1960).

the balance of evidence suggests that the hydrogen is most likely to be in the form of a negative ion as a first approximation. In principle, approaches along these lines could be useful in providing a broad framework to compare and account for differences in the extent of absorption of hydrogen by many different metals over a range of experimental conditions. For instance, this seems one possible means of correlating the experimental p–C–T relationships of the nickel/hydrogen system (Baranowski and Bocienska, 1965) and of the apparently complicated manganese/hydrogen system (Sieverts and Moritz, 1937; also Smith, 1948) where the isobaric solubility (under a pressure of 1 atm H_2) decreases with increasing temperature up to ~300°, but then increases again at still higher temperatures.

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The numbers on the right-hand margin in square brackets refer to the page or pages in the text where mention of a given work or person is made.

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[redacted]		APR 1 1 1999	
[redacted]			
[redacted]			
DEC 1 8 1998		[redacted]	
JAN 2 2 1999			
[redacted]			
			Printed in USA

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